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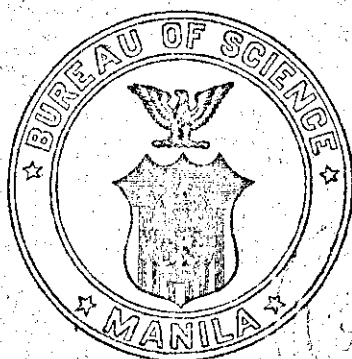
# THE PHILIPPINE JOURNAL OF SCIENCE

ALVIN J. COX, M. A., PH. D.  
GENERAL EDITOR

## SECTION A CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

EDITED WITH THE COÖPERATION OF

W. E. PRATT, A. M.; R. R. WILLIAMS, M. S.; D. S. PRATT, PH. D.  
J. R. WRIGHT, PH. D.; H. C. BRILL, PH. D.; G. W. HEISE, M. S.  
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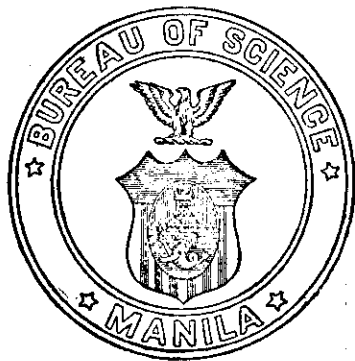
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WITH 30 PLATES AND 40 TEXT FIGURES



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# THE PHILIPPINE JOURNAL OF SCIENCE

A. CHEMICAL AND GEOLOGICAL SCIENCES  
AND THE INDUSTRIES

VOL. X

JANUARY, 1915

No. 1

## PAPAIN: ITS COMMERCIAL PREPARATION AND DIGESTIVE PROPERTIES

By DAVID S. PRATT

(From the Laboratory of Organic Chemistry, Bureau of Science,  
Manila, P. I.)

TWO PLATES AND 4 TEXT FIGURES

Papain is the name usually given to the proteolytic enzyme elaborated by *Carica papaya* L. and secreted in the milky latex that forms a prominent characteristic of the plant. The papaya tree is normally an erect plant, from about 5 to 10 meters in height at maturity, seldom branched, with a soft trunk and a crown of large palmately lobed leaves. The plentiful fruits are melon shaped, up to 40 centimeters in length, with a golden-orange pulp and numerous small black seeds. They are used to a large extent in many tropical countries as a refreshing food, although possessing little actual nutritive value.<sup>1</sup>

The name papaya is said to have been derived from the Carib *ababai*, and has been further altered to the term *papaw*. The plant is a native of the Caribbean Gulf of Mexico, and South America, and has spread to many parts of the world. It was introduced into the Philippines in the seventeenth century, and has been cultivated since. Suitable conditions for its growth exist in many other countries, among which the Hawaiian Islands, Assam, Ceylon, and the Philippine Islands deserve special mention.

Various medicinal uses of papaya have been known for many

<sup>1</sup> Pratt and del Rosario, *This Journal*, Sec. A (1913), 8, 69.

years. The Caribs have long employed the ripe fruit as a cosmetic, and the remarkable complexions of these people are attributed to the use of the pulp as a skin soap. It is also said to remove freckles, and is frequently used by the natives of Ceylon as a soap to remove stains and to intensify colors, especially black, in washing fabrics. The juice is used in the Antilles as a poultice in the treatment of ulcers, sores, yaws, and other skin diseases, and I found similar application made of it by Singhalese who reported very beneficial results. Antiaphrodisiac properties are frequently ascribed to the papaya by the natives of Ceylon, and a similar superstition is widespread in the Philippines. The well-authenticated action of sliced green fruit in softening meat is known to native cooks in many countries both in Central America and in Asia. Griffith Hughes noted this custom in 1750 when he wrote in his *History of Barbadoes*, "The juice is of so penetrating a nature, that if the unripe fruit when unpeeled is boiled with the toughest old salt meat, it will soon make it soft and tender." European residents of the tropics are familiar with the important beneficial results of eating ripe papaya. Obstinate cases of dyspepsia and constipation yield readily to the pleasant and simple expediency of including a papaya in the breakfast menu. I have personally known of a sufficient number of such instances to leave no doubt in this respect.

All of these properties are to be attributed to the presence of papain. The latex containing this enzyme is present in all parts of the plant, and exudes from the slightest injury. It is found to the greatest extent in a network of circulatory vessels beneath the surface of unripe fruits, and is collected in commercial quantities by scarifying such papayas. The fresh latex is dried to the consistency of gum and shipped in a crude state, principally to London and Hamburg, whence it is largely re-exported to the United States.

The bulk of papain at the present time is produced in the West Indies, followed by Mexico and Ceylon, although the last produces the largest amount of gum. I recently had the opportunity of witnessing Singhalese gather the papaya latex for shipment. A casual inspection of the primitive methods employed in the Kegalle district, whence the greater part of Ceylon gum is obtained, sufficed to explain why so much unjust criticism has been made regarding the use of papain in medicine and why many physicians have become sceptical of its value as a substitute for pepsin. A brief descrip-

tion of the general procedure from tapping the fruit to export of the gum should be of interest.

Kegalle is situated between Colombo and the Royal Botanic Gardens at Paradeniya, with an annual rainfall of from 190 to 250 centimeters and with soil conditions well adapted to the growth of papayas. Gathering and drying the latex is entirely in the hands of ignorant natives, who are not capable of appreciating the care and cleanliness which should always be employed in dealing with a sensitive material, such as an enzyme. Good results cannot be expected, and it is rather surprising that the final product shows any proteolytic activity, especially as gross adulteration is the rule rather than the exception. The papaya trees are not planted with any degree of regularity, but are found scattered through coconut and areca-palm groves. They receive neither cultivation nor care, but in spite of difficulties continue to bear fruit and support a rather numerous population.

Preparations for gathering latex are very simple, and consist in cutting and forming the leaf sheath of an areca-palm leaf into a shallow basket. A crossbar is tied to the papaya tree at a convenient height, and the basket is hung beneath the unripe fruit, in which slight cuts are made longitudinally, whereupon the milky juice exudes and drops into the basket. The flow is rapid for a few seconds, but becomes slower and slower as the latex coagulates, until it ceases entirely. The jellylike fragments adhering to the fruit are scraped off with a paddle cut from a leafstalk and added to the contents of the basket which are stirred for a few minutes until coagulation takes place (Plate I). It is a common practice to add boiled rice starch at this point for the purpose of increasing the weight and lightening the final color of the gum, the amount of adulterant varying from about 10 to as much as 80 per cent. Other extraneous material, such as clay, bread crumbs, dried fruit, and India rubber latex, are occasionally used.

The juice is now spread out on papers in the sun to dry, three or four days generally being sufficient for the purpose. On several occasions, I noticed papers of partially dried gum exposed to clouds of dust and dirt from near-by thoroughfares. The color gradually darkens as the drying proceeds, until the final product is brown to nearly black in the case of straight gum or light brown when large percentages of starch have been added. The gum is sold in Colombo to Colombo brokers as No. 1 and is marketed in the markets demand a light-colored 1 grade. Pure gum, light in



color and of high activity, could hardly be made by the native process outlined above. An attempt is, therefore, made to meet the requirements of London and Hamburg dealers by blending No. 1 with No. 2. This gives No. 2 mixed (Plate II). The two components may readily be recognized in such a mixture, as the individual lumps are large enough to render separation by hand picking a simple matter. The effect of this blending is to lighten the color considerably, but at the same time very greatly to decrease the activity of the gum. It will be shown later that the light-brown fragments of highly adulterated gum are practically inert, and as this grade frequently comprises from 30 to 50 per cent of an entire shipment it may be seen how seriously the product is injured. Many dealers in Colombo informed me that they were adverse to blending the two grades of papain in this manner, but that dark-colored No. 1 was unsalable and pure light-brown gum could not be made. The latter statement does not correctly represent the situation, as Mexican papain is lighter in color and the West Indian product resembles dried bread crumbs.

Further difficulties have arisen during the past year. Many shipments of Colombo No. 2 mixed have been refused admittance by the United States customs, because adulterated with starch although invoiced as papain. Thus the sale of Ceylon papaya gum has decreased considerably, but various brokers who have dealt in this product for many years informed me that they could readily sell at least a ton per month of high-grade papain provided it were free from adulteration and light colored. Quotations from various drug houses in the United States indicate that properly prepared gum would find a ready market at prices ranging from 11 to 13 pesos per kilogram (2.50 to 3 dollars per pound).

This investigation was undertaken for the purpose of comparing papaya gums made in a variety of ways and, especially, to ascertain whether it was possible to conserve the entire efficiency of fresh latex by employing proper methods for drying. Various means for determining the digestive value of papain have been suggested from time to time, and many firms handling the gum employ arbitrary standards based upon what they consider a satisfactory preparation. Grated finely ground steak in dilute hydrochloric acid toe<sup>3</sup> prefe

<sup>3</sup> *Journ. Ind. & Eng.*

<sup>3</sup> *Ibid.* (1912), 4, 51

coagulated egg albumen in 0.10 per cent sodium hydroxide solution, while others advocate fibrin, etc. The duration and temperature employed also vary greatly. No systematic investigations have been made that enable one to form a logical opinion regarding the digestive powers of papain; the optimum conditions of temperature, alkalinity, or acidity; the rate of digestion; etc.

It was greatly to be desired that some method for analysis be found which would give accurate results without requiring elaborate apparatus or laborious manipulation and that would not depend upon some sample of papaya gum arbitrarily selected as a standard. Methods depending upon the comparative volumes of undigested material are not trustworthy, and those in which it is necessary to determine the increase in soluble nitrogen during digestion are not only unsatisfactory, but also exceedingly tedious when many analyses have to be made.

The following scheme for assaying papain has given satisfactory results in many hundreds of cases, and may be recommended as simple, rapid, and accurate. It has the advantage of being carried out readily in any laboratory, and gives all the information necessary for determining the quality of the sample.

#### METHOD FOR THE ANALYSIS OF PAPAIN

Milk, as nearly as possible free from butter fat, is the most satisfactory material to employ as substrate. The various well-known brands of condensed skimmed milk possess reasonably constant composition, and are well suited to the purpose. I employed a 40 per cent solution of sweetened condensed skimmed milk in the analyses recorded in this paper, not only because fresh skimmed milk was not procurable in Manila, but also for the reason that the canned milks keep well and are thus always available.

The enzyme solution was prepared by dissolving 0.75 gr of powdered papain in 150 cubic centimeters of distilled water. Papain is not completely soluble in water, but by warm mixture for thirty minutes in the thermostat at 40° C principle is dissolved and upon filtering a clear solution is obtained. Well-prepared gums give a colorless filtrate slightly acid and shows a marked tendency to form precipitates. Digestions were carried out in 150 cubic centimeter flasks. The volumes of milk, water, and papain may be seen from Table I.

TABLE I.—*Typical digestion experiment.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.
	cc.	cc.	cc.	mg.
1	25	23	2	10
2	25	21	4	20
3	25	19	6	30
4	25	17	8	40
5	25	15	10	50
6	25	13	12	60
7	25	11	14	70
8	25	9	16	80
9	25	7	18	90
10	25	5	20	100
11	25	25	0	0

The milk and water were always measured into the flasks and mixed by shaking. The enzyme solution was rapidly added from a burette, the contents were well mixed by a few vigorous shakes, and the flasks were at once placed in the thermostat. At the expiration of exactly thirty minutes they were removed in the same order, 20 cubic centimeters of ice water added to each, and the flasks placed in melting ice to stop digestion.

The contents of each flask were then successively washed into a 500 cubic centimeter beaker, sufficient water being used to give approximately 75 cubic centimeters of final volume. The undigested protein was then precipitated by slowly adding 0.5 cubic centimeter of copper sulphate solution (60 grams per liter), followed by 0.5 cubic centimeter of glacial acetic acid, the solution being vigorously stirred during precipitation.

The contents of the beaker were now washed into 100 cubic centimeter measuring cylinders and allowed to stand for a short time to permit the curd to settle, after which they were filtered through 11-centimeter ashless papers, which had been previously numbered, dried at 100°, and weighed. It frequently happens filtration proceeds very slowly, in which case it is not possible to wait until all the liquid has passed through, but to proceed with the washing. The curd is washed back into cylinders with distilled water warmed to about 60°, roughly disintegrated by means of a rubber-tipped rod. The sediment now settles readily, and the solutions are decanted. The undigested protein is washed three more times in the same manner to remove sugars and soluble digestion products. Suction is applied to remove the surplus water,

and the papers are dried to constant weight at 100°. No correction for the amount of papain used is necessary, as it is not precipitated by copper sulphate and acetic acid.

The weight of protein digested by the various amounts of papain may be calculated from the blank in which no enzyme was used. The entire determination with the exception of drying may be made in from three to four hours, and duplicate analyses agree within about 2 per cent. The curves obtained in this manner show at a glance the relative proteolytic power possessed by samples of papain, as well as the rate at which digestion has proceeded with increasing amounts of enzyme. No antiseptic is necessary with such short periods of incubation.

Analyses were carried out in this manner with commercial samples of papain from various sources. A great divergence in activity was encountered, ranging from gum possessing practically no proteolytic power to highly active material. The curves obtained from these data are plotted in fig. 1.

#### ANALYSES OF PAPAIN

*No. 1. Papain from local drug store.*—This sample was of unknown origin, and had been obtained from Germany several years previously. It was light colored, and possessed an odor resembling pepsin. A small portion boiled with water gave a positive test for starch with iodine solution. The analysis is shown in Table II.

TABLE II.—Analysis of papain, sample 1.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,160	0	0.0	-----
2	25	21	4	20	1,163	0	0.0	-----
3	25	19	6	30	1,159	0	0.0	-----
4	25	17	8	40	1,151	4	0.3	0.1
5	25	15	10	50	1,149	6	0.5	0.1
6	25	13	12	60	1,132	22	1.9	0.3
7	25	11	14	70	1,116	39	3.4	0.5
8	25	9	16	80	1,107	48	4.2	0.5
9	25	7	18	90	1,098	57	5.0	0.6
10	25	5	20	100	1,092	63	6.0	0.6

Protein in blank = 1,155 milligrams.

Acidity of papain solution as HCl = 0.005 per cent.

The sample was practically inert; although it retailed at 1 peso (50 cents) per 20 grams.

No. 2. *Ceylon papain. Grade 2.*—I obtained this sample from the warehouse of a prominent broker in Colombo, who informed me that it represented the usual quality of the light-colored, highly adulterated grade. The analysis is shown in Table III.

TABLE III.—Analysis of second-grade Ceylon papain, sample 2.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,119	1	0.1	0.1
2	25	21	4	20	1,111	9	0.1	0.4
3	25	19	6	30	1,120	0		
4	25	17	8	40	1,121	0		
5	25	15	10	50	1,104	18	1.4	0.3
6	25	13	12	60	1,069	51	4.6	0.8
7	25	11	14	70	1,093	27	2.4	0.4
8	25	9	16	80	1,086	34	3.0	0.4
9	25	7	18	90	1,101	19	1.2	0.2
10	25	5	20	100	1,107	13	1.2	0.1

Protein in blank=1,120 milligrams.

Starch present in large amounts.

Practically inert.

No. 3. *Ceylon papain. Grade 1.*—This sample was from the same source as the preceding. It was chocolate colored and non-friable. The analysis is shown in Table IV.

TABLE IV.—Analysis of grade 1, Ceylon papain, sample 3.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,064	56	5.0	5.6
2	25	21	4	20	996	124	11.1	6.2
3	25	19	6	30	890	230	20.6	7.6
4	25	17	8	40	885	235	21.0	5.8
5	25	15	10	50	858	262	23.4	5.2
6	25	13	12	60	827	293	26.2	4.9
7	25	11	14	70	789	331	29.6	4.7
8	25	9	16	80	743	372	33.2	4.6
9	25	7	18	90	720	400	35.7	4.4
10	25	5	20	100	674	446	39.8	4.0

Protein in blank=1,120 milligrams.

Starch present.

Acidity of papain solution as HCl=0.008 per cent.

The activity is not high, and the ratio is very low even with small amounts of gum.

No. 4. *Ceylon papain*.—I obtained this sample from another prominent dealer in Colombo. It closely resembled the preceding in appearance, and was considered as unadulterated. The analysis is shown in Table V.

TABLE V.—Analysis of *Ceylon papain*, sample 4.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,033	96	8.5	9.6
2	25	21	4	20	943	186	16.5	9.3
3	25	19	6	30	877	252	22.4	8.4
4	25	17	8	40	802	327	23.0	8.2
5	25	15	10	50	759	370	32.8	7.4
6	25	13	12	60	717	412	36.5	6.9
7	25	11	14	70	688	441	39.1	6.3
8	25	9	16	80	645	484	42.8	6.1
9	25	7	18	90	612	517	45.9	5.7
10	25	5	20	100	589	540	48.0	5.4

Protein in blank=1,129 milligrams.

Starch absent.

Acidity of papain solution as HCl=0.004 per cent.

No. 5. *Ceylon papain*.—This sample was from the same source as No. 4 and is similar in appearance, but it contains starch as adulterant. The analysis is shown in Tables VI and VII.

TABLE VI.—Analysis of *Ceylon papain*, sample 5.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,156	57	4.7	5.7
2	25	21	4	20	1,112	101	8.3	5.0
3	25	19	6	30	1,087	126	10.4	4.2
4	25	17	8	40	1,035	178	14.7	4.4
5	25	15	10	50	995	218	18.0	4.4
6	25	13	12	60	933	280	23.1	4.6
7	25	11	14	70	937	276	22.8	3.9
8	25	9	16	80	878	335	27.6	4.2
9	25	7	18	90	850	353	29.9	4.0
10	25	5	20	100	808	405	33.3	3.3

Protein in blank=1,213 milligrams.

Starch present.

Acidity of papain solution as HCl=0.003 per cent.

TABLE VII.—Duplicate analysis of Ceylon papain, sample 5.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,158	70	5.7	7.0
2	25	21	4	20	1,128	100	8.2	5.0
3	25	19	6	30	1,112	116	9.5	3.8
4	25	17	8	40	1,036	192	15.7	4.8
5	25	15	10	50	997	231	13.8	4.6
6	25	13	12	60	981	247	20.2	4.1
7	25	11	14	70	962	266	21.7	3.8
8	25	9	16	80	941	287	23.4	3.6
9	25	7	18	90	896	332	27.1	3.7
10	25	5	20	100	811	417	34.0	3.4

This is a duplicate analysis of sample 5, and is included to show how close agreement may be expected when dealing with low-grade gums.

*No. 6. Ceylon papain.*—This sample was obtained from Mead Johnson and Company, Jersey City, U. S. A. It is considerably lighter in color than the preceding, being approximately a mean between grades 1 and 2. The analysis is shown in Table VIII.

TABLE VIII.—Analysis of Ceylon papain, sample 6.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	941	220	19.0	22.0
2	25	21	4	20	790	371	31.9	18.6
3	25	19	6	30	697	464	40.0	15.4
4	25	17	8	40	614	547	47.2	13.7
5	25	15	10	50	532	629	54.3	12.6
6	25	13	12	60	482	679	58.5	11.3
7	25	11	14	70	451	710	61.3	10.1
8	25	9	16	80	412	749	64.6	9.4
9	25	7	18	90	383	778	67.1	7.4
10	25	5	20	100	365	796	68.6	6.9

Protein in blank=1.161 milligrams.

Starch absent.

Acidity of papain solution as HCl=0.007 per cent.

Mead Johnson & Co. states that this is an unusually light-colored specimen of Ceylon gum.

*No. 7. Ceylon papain.*—This sample was obtained from Mead Johnson and Company. It consists of both dark- and light-colored fragments, and may be classified as grade 2 mixed. The results of the analysis are shown in Table IX.

TABLE IX.—Analysis of Ceylon papain, sample 7.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,179			
2	25	21	4	20	1,144	35	3.0	1.8
3	25	19	6	30	1,155	28	2.0	0.7
4	25	17	8	40	1,129	50	4.2	1.2
5	25	15	10	50	1,106	73	6.2	1.4
6	25	13	12	60	1,134	45	3.8	0.8
7	25	11	14	70	1,097	82	7.0	1.2
8	25	9	16	80	1,100	79	6.7	1.0
9	25	7	18	90	1,073	106	9.0	1.2
10	25	5	20	100	1,036	143	12.2	1.2

Protein in blank=1,179 milligrams.

Starch present in large amount.

Acidity of papain solution as HCl=0.001 per cent.

Regarding this sample Mead Johnson & Co. states that it is a good specimen of the product usually handled by drug brokers. The above analysis shows how little value it actually possesses.

**No. 8. Mexican papain.**—This sample was obtained from Mead Johnson and Company. It was approximately the color of sample 6, and showed a comparatively uniform composition. The results of the analysis are shown in Table X.

TABLE X.—Analysis of Mexican papain, sample 8.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,090	129	6.5	12.9
2	25	21	4	20	1,009	210	17.2	10.5
3	25	19	6	30	956	263	21.6	8.8
4	25	17	8	40	889	330	27.1	8.3
5	25	15	10	50	804	415	34.0	8.3
6	25	13	12	60	772	447	36.7	7.5
7	25	11	14	70	734	485	39.8	6.9
8	25	9	16	80	698	521	42.7	6.5
9	25	7	18	90	660	559	45.8	6.2
10	25	5	20	100	645	574	47.1	5.7

Protein in blank=1,219 milligrams.

Starch absent.

Acidity of papain solution as HCl=0.005 per cent.

Mead Johnson & Co. states that this is unusually dark colored for Mexican gum, which should more resemble the West Indian product.



No. 9. *West Indian papain*.—This sample was obtained from Mead Johnson and Company. It was a light biscuit color, readily friable, and of uniform appearance. The analysis is given in Table XI.

TABLE XI—Analysis of West Indian papain, sample 9.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	815	400	32.9	40.0
2	25	21	4	20	697	518	42.7	25.9
3	25	19	6	30	593	622	51.2	20.7
4	25	17	8	40	458	757	62.6	18.9
5	25	15	10	50	416	799	65.8	16.0
6	25	13	12	60	343	872	71.8	14.5
7	25	11	14	70	295	920	75.8	13.1
8	25	9	16	80	271	944	77.8	11.8
9	25	7	18	90	251	964	79.8	10.7
10	25	5	20	100	243	972	80.0	8.0

Protein in blank=1,215 milligrams.

Starch absent.

Acidity of papain solution as HCl=0.005 per cent.

Mead Johnson & Co. states that it regards West Indian gum as the best produced, and this view is clearly substantiated by the above analysis.

The results of the above analyses are plotted in fig. 1, where the various curves show not only the percentage of total protein digested by increasing amounts of papain, but also give graphically a clear idea of the marked differences existing in the proteolytic activity of the samples, whose numbers are given. Thus, the amount of milk protein digested in thirty minutes at 40° by 1 milligram of West Indian papain is seen to exceed that digested under similar conditions by 100 milligrams of sample 7, representing ordinary Ceylon papain.

#### PREPARATION OF PAPAIN

Various methods for converting fresh latex into dry papain were investigated, in order to ascertain the extent of deterioration during drying and the possibility of preparing papain commercially which would exceed the West Indian product in its proteolytic activity. The fresh latex for this work was obtained under my personal supervision.

Green fruits were scarified with steel knives in the usual

manner, and the juice was collected in porcelain evaporating dishes. The entire collection, amounting to approximately 0.5 kilogram, was thoroughly mixed to insure uniform composition, using a bone spatula, and was divided into various portions

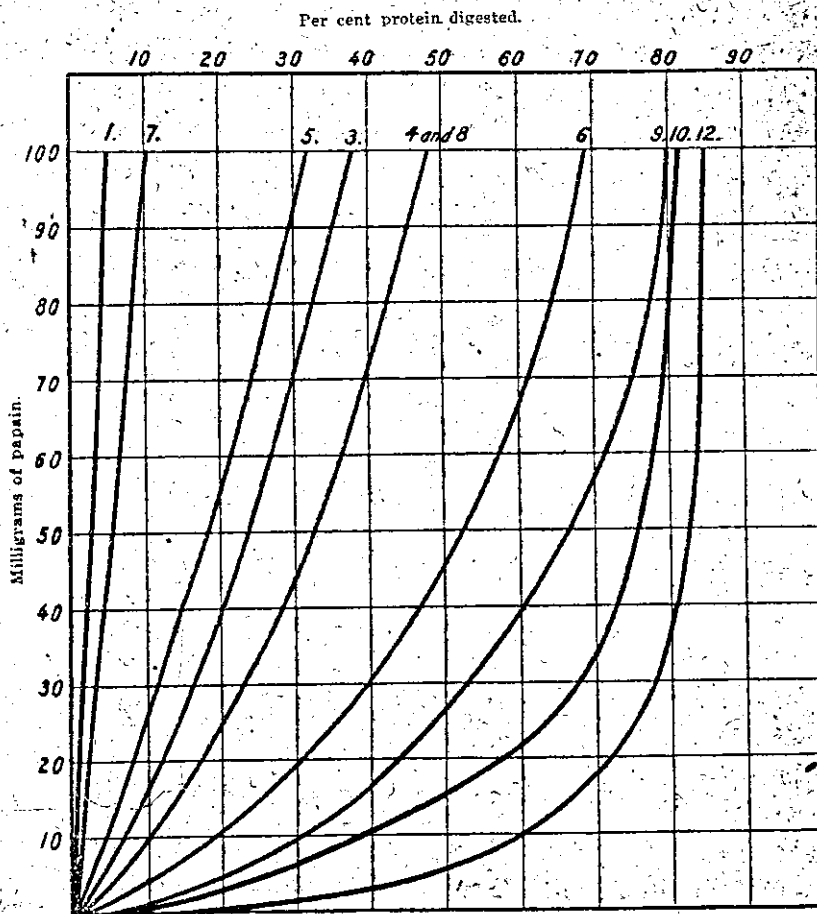


FIG. 1. Curve 1. Papain from local drug store. Curve 3. Ceylon papain, sample 3. Curve 4. Ceylon papain, sample 4. Curve 5. Ceylon papain, sample 5. Curve 6. Ceylon papain, sample 6. Curve 7. Ceylon papain, sample 7. Curve 8. Mexican papain, sample 8. Curve 9. West Indian papain, sample 9. Curve 10. Fresh papaya latex, sample 10. Curve 11. Papain by alcohol precipitation, sample 11. Curve 12. Papain by alcohol precipitation, sample 12.

which were treated in different ways. The activity of original latex designated No. 10 was obtained by analysis the above manner, the weight of latex used being compared to dry papain. The results of the analysis are shown in Table XII.

TABLE XII.—Analysis of fresh papaya latex, sample 10.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	702	458	39.6	45.8
2	25	21	4	20	473	687	59.2	34.4
3	25	19	6	30	338	822	71.0	27.4
4	25	17	8	40	312	848	73.3	21.2
5	25	15	10	50	277	883	76.3	17.7
6	25	13	12	60	257	903	77.8	15.1
7	25	11	14	70	244	916	79.0	13.1
8	25	9	16	80	230	930	80.3	11.7
9	25	7	18	90	212	943	81.7	10.5
10	25	5	20	100	212	948	81.7	9.5

Protein in blank=1,160 milligrams.

Acidity of enzyme solution as HCl=0.006 per cent.

The relationship between enzyme and percentage of protein digested in thirty minutes at 40° is plotted as curve 10 in fig. 1. It is evident that the fresh latex is considerably more active than dried papain from the Antilles, although both preparations are capable of digesting approximately the same amount of milk protein with relatively large amounts of enzyme present. The curve for fresh latex shows a rapid increase in digestion with increasing amounts of papain up to about 20 milligrams corresponding to 58 per cent digestion of the total protein content, while the West Indian papain gives only 44 per cent digestion at this concentration.

A portion of the fresh latex was spread out in a porcelain dish to form a thin layer and was sundried. It was frequently stirred, and the gummy lumps were sliced to facilitate the rapid evaporation of moisture. The color darkened slightly, and approximated that shown by the West Indian papain. The product designated No. 11 was readily friable when thoroughly dry, and gave the analysis shown in Table XIII.

The results of this analysis are not plotted, as the curve closely approximates that given by fresh latex. The central portion shows somewhat less digestion, the maximum divergence being about 3 per cent with 40 milligrams of papain. It thus appears that sundried papain is not necessarily less active than fresh latex, but in this case it must be remembered that considerable care was given the sample to insure rapid drying, exclusion of dust, etc. It was also dried promptly after collection. This is very important, as fermentation takes place

TABLE XIII.—Analysis of sundried Philippine papain, sample 11.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	701	454	39.4	45.4
2	25	21	4	20	510	645	55.8	32.3
3	25	19	6	30	404	751	65.0	25.0
4	25	17	8	40	347	808	70.0	20.2
5	25	15	10	50	308	847	73.5	16.9
6	25	13	12	60	278	877	76.0	14.6
7	25	11	14	70	259	896	77.7	12.8
8	25	9	16	80	249	906	78.5	11.3
9	25	7	18	90	235	920	79.6	10.2
10	25	5	20	100	203	952	82.5	9.5

Protein in blank=1.155 milligrams.

Acidity of papain solution as HCl=0.008 per cent.

rapidly in papaya latex with the production of nauseating odors and destruction of the enzyme.

Small portions of the fresh latex were dried rapidly in vacuo over sulphuric acid. The resulting papain was a light cream color, was easily friable, and upon analysis showed little if any difference in activity from the original. The chief advantages resulting from drying in this manner are the shortness of the time required, lighter color, and more porous nature of the resulting papain. Its successful application on a large scale would necessitate special machinery, whereby the latex might be thoroughly stirred during drying. Further difficulties would arise from the gummy consistency of the partially dried product and the necessity of avoiding contact with metals that cause darkening of the color.

Many enzymes may be purified and separated from extraneous material by precipitation with alcohol. This method is applicable to papaya latex, and gives excellent results provided the action of the alcohol is limited to as short a time as possible.

Twenty grams of the fresh latex were well mixed with 100 cubic centimeters of 95 per cent alcohol. A gummy white coagulum was thrown down that was readily collected in a ball. The alcohol was poured off and replaced with 50 cubic centimeters of the same strength. The papain readily crumbled to a fine powder during the second treatment with alcohol. It was filtered with suction and washed twice with ether to remove solid yellow wax and to facilitate drying. The was

papain was dried in vacuo, giving a perfectly white powder with a faint characteristic odor; yield, 3 grams. The time required from latex to dry papain was about twenty minutes. An analysis of this product designated No. 12 is shown in Table XIV.

TABLE XIV.—Analysis of Philippine papain, sample 12.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	451	722	61.5	72.2
2	25	21	4	20	330	843	71.8	42.1
3	25	19	6	30	266	907	77.3	30.2
4	25	17	8	40	234	939	80.0	23.5
5	25	15	10	50	224	949	81.0	19.0
6	25	13	12	60	196	977	83.2	16.3
7	25	11	14	70	183	990	84.5	14.1
8	25	9	16	80	185	988	84.0	12.3
9	25	7	18	90	182	991	84.5	11.0
10	25	5	20	100	175	998	85.3	10.0

Protein in blank = 1,173 milligrams.

Acidity of papain solution as HCl = 0.004 per cent.

The results of this analysis are plotted in fig. 1 as curve 12. It may be seen that this sample of papain is very active, 10 milligrams being capable of digesting as much milk protein as 22 milligrams of the Philippine sundried papain or 40 milligrams of the West Indian product. This probably represents the most active papain that could be prepared commercially. Its manufacture by this method would necessitate a still for recovering the waste alcohol. The use of ether would hardly be practical in tropical countries, but could be employed by drug firms using papain, if desirable.

Papain prepared in this manner is nearly soluble in water, giving an opalescent solution with small flocks of white insoluble material. The solution rapidly curdles milk, with the formation of a fine curd that quickly redissolves. This property of papain should make it of great value in preparing milk for infant feeding, as the formation of heavy indigestible curds in the stomach may thus be avoided.

#### RATE OF DIGESTION

All of the preceding digestions were carried out at 40° for a period of thirty minutes. The following experiment was made to determine the rate at which milk protein is digested by

pain. All of the flasks contained the same amounts of milk, water, and enzyme solution, but were maintained at 40° for varying lengths of time before precipitation. The results of this series are shown in Table XV. The papain used was sample 6 from Ceylon.

TABLE XV.—Rate of digestion of milk protein.

No. of flask.	Time of digestion.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	Mins.	mg.	mg.	Per cent.	
1	10	862	281	24.7	11.2
2	20	816	327	28.6	13.1
3	30	783	360	31.5	14.4
4	40	760	383	33.5	15.3
5	50	741	402	35.1	16.0
6	60	714	429	37.5	17.0
7	70	703	440	38.4	17.6
8	80	702	441	38.5	17.6
9	90	708	435	38.1	17.4
10	100	664	479	41.8	19.1
11	110	685	453	40.1	18.0
12	120	675	468	40.9	18.7
13	130	681	462	40.3	18.5
14	140	668	475	41.6	19.0
15	150	658	485	42.4	19.4

Protein in blank=1,143 milligrams.

Each flask contained 25 cubic centimeters of milk, 20 cubic centimeters of water, and 5 cubic centimeters of enzyme solution equivalent to 25 milligrams of papain.

These results are plotted in fig. 2. An inspection of this curve shows that digestion proceeded rapidly during the first ten minutes and practically reached its maximum within an hour. The nature of the protein and conditions of solution, concentration, etc. would affect the equilibrium to a greater or less extent, so that this period of digestion must not be taken as applying to some other substrate, such as beef.

#### DIGESTION UNDER VARIOUS CONDITIONS

The literature of papain contains many conflicting statements regarding the conditions suitable for digestion. Some authors claim that the enzyme acts in neutral, alkaline, or acid solution; others, that one or the other is best suited for proteolytic activity. The question is important in its bearing upon the use of papain as a medicinal agent and interesting in comparing papain with other enzymes, such as pepsin and trypsin.

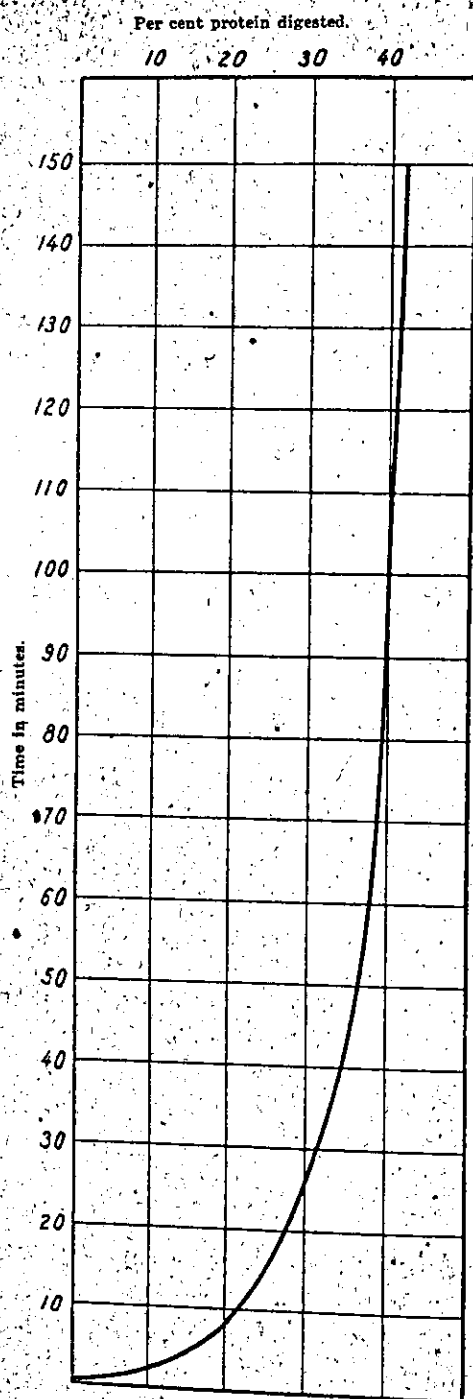


FIG. 2. Rate of digestion of milk protein by papain.

## PAPAIN DIGESTION IN ACID SOLUTION

The following experiments were made to determine the effect of hydrochloric acid on the digestion of milk protein. The digestions were carried out in the usual manner for thirty minutes at 40°. The results are shown in Table XVI.

TABLE XVI.—*Papain digestion of milk protein in acid solution.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Hydrochloric acid solution.	Hydrochloric acid.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	cc.	Per cent.	mg.	mg.	Per cent.	
1	25	15	10	50	0	0.00	651	505	43.7	10.1
2	25	14	10	50	1	0.02	671	485	42.0	9.7
3	25	13	10	50	2	0.04	670	486	42.0	9.7
4	25	12	10	50	3	0.06	719	437	37.8	8.7
5	25	11	10	50	4	0.08	750	406	35.1	8.1
6	25	10	10	50	5	0.10	838	318	27.6	6.4
7	25	9	10	50	6	0.12	946	210	13.2	4.2
8	25	8	10	50	7	0.14	982	174	15.1	3.5
9	25	7	10	50	8	0.16	998	158	13.7	3.2
10	25	6	10	50	9	0.18	1,000	156	13.5	3.1
11	25	5	10	50	10	0.20	1,003	153	13.2	3.1

Protein in blank=1,156 milligrams.

TABLE XVII.—*Papain digestion of milk protein in acid solution.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Hydrochloric acid solution.	Hydrochloric acid.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	cc.	Per cent.	mg.	mg.	Per cent.	
1	25	20	5	25	0	0.00	951	250	20.8	10.0
2	25	19	5	25	1	0.02	951	250	20.8	10.0
3	25	18	5	25	2	0.04	974	227	18.9	9.1
4	25	17	5	25	3	0.06	989	212	17.7	8.5
5	25	16	5	25	4	0.08	1,004	197	16.4	7.9
6	25	15	5	25	5	0.10	1,060	141	11.8	5.6
7	25	14	5	25	6	0.12	1,110	91	7.6	3.6
8	25	13	5	25	7	0.14	1,115	86	7.2	3.4
9	25	12	5	25	8	0.16	1,123	78	6.5	3.1
10	25	11	5	25	9	0.18	1,136	65	5.4	2.6
11	25	10	5	25	10	0.20	1,138	63	5.3	2.5

Protein in blank=1,201 milligrams.

The results of this experiment are plotted as curve 1 in fig. 3. This curve shows that amounts of hydrochloric acid up to 0.06 per cent have only a slight retarding action on the digestion of milk protein. Increasing amounts from 0.06 to 0.13 per cent acid very greatly reduce the activity of the enzyme,



although any further increase up to 0.20 per cent causes practically no change. A sharply defined range of acidity thus reduces the digestion to one-half its former value. One more example

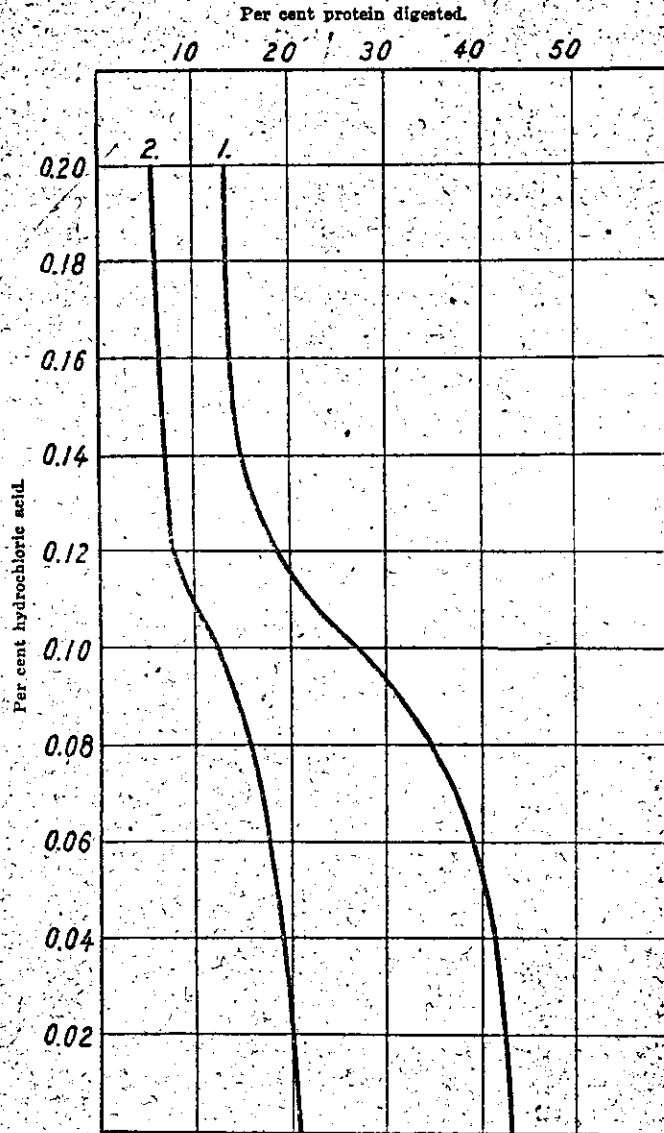


FIG. 3. Digestion in hydrochloric acid solution. Curve 1. With 50 milligrams of papain.  
Curve 2. With 25 milligrams of papain.

of digestions under similar conditions, but with a less amount of papain, will serve to show the same peculiar effect.

The results are plotted as curve 2 in fig. 3. It will be noticed that the two curves are entirely analogous and that the percent-

age of protein digested by 25 milligrams of papain is almost exactly half that found with 50 milligrams at corresponding points on the curves. In all cases, the mineral acid was neutralized by an equivalent amount of sodium hydroxide solution immediately before precipitating with copper sulphate and acetic acid. Otherwise, milky solutions are encountered that will not permit filtration.

The peculiar transition point in these curves was thought to indicate the appearance of uncombined hydrochloric acid, but such is not the case. A similar series was prepared for the purpose of determining free acid by titration, using Topfer's reagent (dimethylamidoazobenzol) as indicator. None of the flasks showed the presence of free acid. The milk in the flasks containing 0.02 per cent acid was not coagulated, that with 0.04 and 0.06 per cent showed slight coagulation, while the remainder was coagulated.

In as much as the enzyme solution had been added after acidification, there was a possibility that the papain acted only as the surface of curds thus formed and that the results, therefore, did not represent the true rate of digestion. This possibility was avoided by adding the enzyme solution to the milk and water before acidifying. All the solutions were maintained at 0° to prevent digestion before the addition of acid. It was impossible to start the digestions as promptly in this manner as in previous cases. The time, therefore, was extended to ninety minutes to compensate for irregularity at the beginning and to insure equilibrium. Papain 6 was used. The results are found in Table XVIII.

TABLE XVIII.—*Papain digestion of milk protein in acid solution.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Hydrochloric acid solution.	Hydrochloric acid.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	cc.	Per cent.	mg.	mg.	Per cent.	
1	25	15	10	50	0	0.00	620	522	45.7	110.4
2	25	14	10	50	1	0.02	617	525	46.0	10.5
3	25	13	10	50	2	0.04	640	502	44.0	0.0
4	25	12	10	50	3	0.06	687	455	39.8	9.1
5	25	11	10	50	4	0.08	747	395	34.5	7.9
6	25	10	10	50	5	0.10	820	322	29.2	6.4
7	25	9	10	50	6	0.12	937	205	18.0	4.1
8	25	8	10	50	7	0.14	987	155	13.6	3.1
9	25	7	10	50	8	0.16	982	160	14.0	3.2
10	25	6	10	50	9	0.18	1,001	141	12.4	2.8
11	25	5	10	50	10	0.20	1,005	137	12.0	2.7

Protein in blank=1,142 milligrams.

The results are practically identical with those given in Table XVI, and show that no different effect is obtained by adding the enzyme solution before coagulation.

Digestion experiments were carried out in solutions containing sodium bicarbonate in amounts ranging from 0.0 to 0.2 per cent. The presence of this alkali had no effect on the digestion of milk protein. Similar negative results were obtained with concentrations of sodium chloride varying from 0.10 to 1.0 per cent, although both of these are said to accelerate the digestion of beef by papain.<sup>4</sup>

#### HYDROCYANIC ACID

Much of the early work that is recorded in the literature of papain must be questioned, because hydrocyanic acid was employed as the antiseptic. It is now known that papain digestion of protein proceeds more rapidly and more completely in the presence of this acid than when toluol or other antiseptic is used. Vines<sup>5</sup> stated that his experiments "strikingly demonstrate the remarkably favourable effect of the presence of HCN upon the proteolytic activity of papain." Mendel and Blood<sup>6</sup> have confirmed this statement in an extended series of experiments with commercial samples of papain, and state that the

accelerating effect [of HCN] is not limited to the hydrolysis of peptone but is also shown in the digestion of raw and coagulated egg-white, fibrin, edestin, and excelsin whether one take as the gauge of digestion the appearance of tryptophane, leucine and tyrosin, the conversion into products not precipitated by hot trichloroacetic acid or the rate of solution of insoluble protein.

No satisfactory explanation of the action of hydrocyanic acid has been advanced. The following series was run with increasing amounts of acid to determine its effect on the digestion of milk protein by pure papain. The enzyme was prepared by the alcohol-precipitation method, and was very active. The data and results are shown in Table XIX.

It may be seen from this table that hydrocyanic acid also increased the percentage of milk protein digested by papain. The ratio increased by about 2 units, although no positive color test with bromine water for tryptophane could be obtained. The presence of 0.02 per cent acid was sufficient to give the maximum effect under these conditions, higher concentrations causing no further increase.

<sup>4</sup> Private communication from L. D. Johnson.

<sup>5</sup> *Ann. Bot.* (1903), 17, 606.

<sup>6</sup> *Journ. Biol. Chem.* (1910), 8, 182.

TABLE XIX.—Effect of hydrocyanic acid on papain digestion of milk protein.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Hydrocyanic acid solution.	Hydrocyanic acid.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	cc.	Per cent.	mg.	mg.	Per cent.	
1	25	15	10	50	0	0.00	270	881	76.5	17.6
2	25	14	10	50	1	0.02	197	954	82.8	19.1
3	25	13	10	50	2	0.04	178	973	84.5	19.5
4	25	12	10	50	3	0.06	196	955	83.0	19.1
5	25	11	10	50	4	0.08	200	951	82.6	19.0
6	25	10	10	50	5	0.10	189	962	83.5	19.2
7	25	9	10	50	6	0.12	181	970	84.2	19.4
8	25	8	10	50	7	0.14	179	972	84.4	19.4
9	25	7	10	50	8	0.16	178	973	84.4	19.4
10	25	6	10	50	9	0.18	179	972	84.4	19.4
11	25	5	10	50	10	0.20	187	964	83.7	19.3

Protein in blank=1.151 milligrams.

Time of digestion, thirty minutes.

Temperature, 40°.

The remarkable effect of hydrocyanic acid was not studied in detail, as it has no bearing on the actual use or preparation of papain. However, the difficulty of obtaining samples of pure papain of known history made it worth while to examine the digestion of peptone under these conditions.

## THE FORMATION OF TRYPTOPHANE FROM WITTE'S PEPTONE

The following mixtures were prepared and incubated at 40°.

*Mixture 1.*

Peptone, 5 per cent	cc.
Papain, 1 per cent	20.0
Water, distilled	20.0
Toluol	0.5

*Mixture 2.*

Peptone, 5 per cent	cc.
Papain, 1 per cent	20.0
Hydrocyanic acid solution, 0.1 per cent	20.0
Toluol	0.5

*Mixture 3, control.*

Peptone, 5 per cent	cc.
Hydrocyanic acid solution, 0.1 per cent	20.0
Water, distilled	20.0
Toluol	0.5

Portions were removed and tested with bromine water for tryptophane. Nos. 1 and 3 gave no color, while No. 2 gave a pronounced purple after twenty-four hours' incubation. These results are in accord with the data given by Mendel and Blood,<sup>\*</sup> working with commercial material.

#### DIGESTION AT VARIOUS TEMPERATURES

Digestions of milk protein were carried out in the usual manner at temperatures ranging from 0° to 70° to determine the activity of papain under these conditions. The papain used in these determinations was prepared by the alcohol precipitation method, and was very active. All digestions were for thirty-minute periods. That at 0° was carried out with all flasks surrounded by finely cracked ice, contained in a well-insulated thermostat. The temperature was not allowed to rise until after the final precipitation with copper sulphate and acetic acid. The analysis is shown in Table XX.

TABLE XX.—*Papain digestion of milk protein at 0°.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	1,102	38	3.3	3.8
2	25	21	4	20	1,048	92	8.1	4.6
3	25	19	6	30	998	147	12.9	4.9
4	25	17	8	40	987	153	13.4	3.8
5	25	15	10	50	922	218	19.1	4.4
6	25	13	12	60	861	279	24.4	4.7
7	25	11	14	70	827	313	27.4	4.8
8	25	9	16	80	817	323	28.4	4.0
9	25	7	18	90	789	351	30.8	3.9
10	25	5	20	100	756	384	33.7	3.4

Protein in blank = 1,140 milligrams.

Papain shows a remarkable activity at low temperatures, as may be seen from the curve in fig. 4 plotted from the above analysis.

The results of a series of digestions run at 10° are shown in Table XXI.

<sup>\*</sup> Loc. cit.

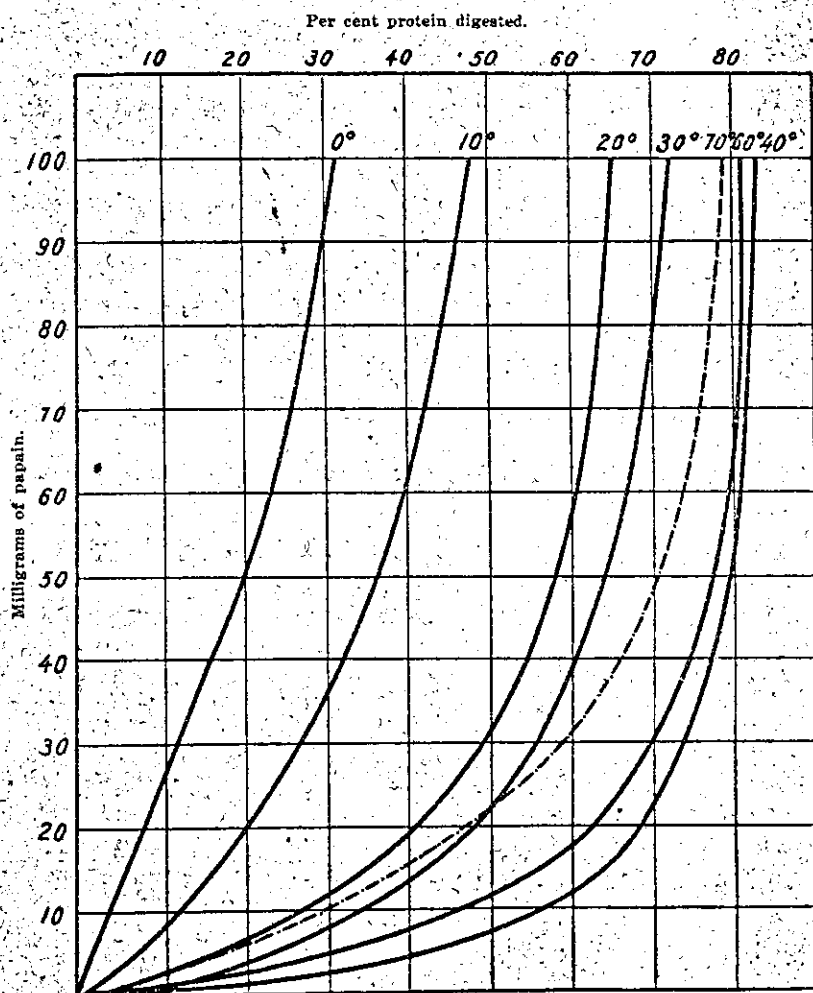


FIG. 4. Digestions at temperatures from 0° to 70°.

TABLE XXI.—*Papain digestion of milk protein at 10°.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	985	155	13.5	15.5
2	25	21	4	20	903	237	20.8	11.9
3	25	19	6	30	827	313	27.4	10.4
4	25	17	8	40	770	370	32.4	9.3
5	25	15	10	50	723	417	36.6	8.3
6	25	13	12	60	685	455	39.9	7.6
7	25	11	14	70	652	488	42.8	7.0
8	25	9	16	80	631	509	44.6	6.4
9	25	7	18	90	605	535	47.0	5.9
10	25	5	20	100	593	547	48.0	5.5

Protein in blank=1,140 milligrams.

The results of a series of digestions run at 20° are shown in Table XXII.

TABLE XXII.—*Papain digestion of milk protein at 20°.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	800	326	29.0	32.6
2	25	21	4	20	648	473	42.6	23.9
3	25	19	6	30	576	550	48.9	18.3
4	25	17	8	40	501	625	55.6	15.6
5	25	15	10	50	469	657	58.4	13.2
6	25	13	12	60	456	670	59.5	11.2
7	25	11	14	70	434	692	61.5	8.9
8	25	9	16	80	412	714	63.4	8.9
9	25	7	18	90	395	731	65.0	8.1
10	25	5	20	100	382	744	66.0	7.4

Protein in blank=1,126 milligrams.

The results of a series of digestions run at 30° are shown in Table XXIII.

The results of a series of digestions run at 40° are shown in Table XXIV.

The results of a series of digestions run at 50° are shown in Table XXV.

The values obtained closely approximate those given in Table XXIV. There appears to be very little difference in the rate of digestion in the neighborhood of 40° to 50°.

TABLE XXIII.—*Papain digestion of milk protein at 30°.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	740	423	36.4	42.3
2	25	21	4	20	533	580	49.8	29.0
3	25	19	6	30	501	662	56.9	22.1
4	25	17	8	40	443	720	61.8	18.0
5	25	15	10	50	409	754	64.8	15.1
6	25	13	12	60	385	778	65.8	13.0
7	25	11	14	70	365	798	68.7	11.4
8	25	9	16	80	340	823	70.6	10.3
9	25	7	18	90	302	861	74.0	9.6
10	25	5	20	100	294	869	74.8	8.7

Protein in blank=1.163 milligrams.

TABLE XXIV.—*Papain digestion of milk protein at 40°.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	483	715	59.6	71.5
2	25	21	4	20	358	840	70.0	42.0
3	25	19	6	30	298	900	75.0	30.0
4	25	17	8	40	275	923	77.0	23.1
5	25	15	10	50	254	944	78.7	18.9
6	25	13	12	60	230	968	80.7	16.1
7	25	11	14	70	223	975	81.3	13.9
8	25	9	16	80	209	989	82.6	12.4
9	25	7	18	90	208	990	82.6	11.0
10	25	5	20	100	202	996	83.0	10.0

Protein in blank=1.126 milligrams.

TABLE XXV.—*Papain digestion of milk protein at 50°.*

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	546	533	51.7	58.3
2	25	21	4	20	367	762	67.7	38.1
3	25	19	6	30	293	836	74.0	27.9
4	25	17	8	40	249	880	78.0	22.0
5	25	15	10	50	223	896	79.5	17.9
6	25	13	12	60	202	927	82.1	15.4
7	25	11	14	70	199	930	82.5	13.3
8	25	9	16	80	191	938	83.0	11.7
9	25	7	18	90	184	945	83.8	10.5
10	25	5	20	100	180	949	84.2	9.5

Protein in blank=1.129 milligrams.



The results of a series of digestions run at 60° are shown in Table XXVI.

TABLE XXVI.—Papain digestion of milk protein at 60°.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	635	529	45.5	52.9
2	25	21	4	20	421	743	63.8	27.1
3	25	19	6	30	327	837	72.0	27.9
4	25	17	8	40	236	878	75.5	22.0
5	25	15	10	50	253	911	78.2	18.2
6	25	13	12	60	241	923	79.3	15.4
7	25	11	14	70	229	935	80.3	13.4
8	25	9	16	80	224	940	80.7	11.8
9	25	7	18	90	214	950	81.6	10.5
10	25	5	20	100	212	952	81.7	9.5

Protein in blank = 1,164 milligrams.

These results show that the optimum temperature has been exceeded, as corresponding values are less than those of Tables XXIV and XXV.

The results of a series of digestions run at 70° are shown in Table XXVII.

TABLE XXVII.—Papain digestion of milk protein at 70°.

No. of flask.	Milk.	Water.	Papain solution.	Papain.	Protein undigested.	Protein digested.	Protein digested.	Parts of protein digested by 1 part papain.
	cc.	cc.	cc.	mg.	mg.	mg.	Per cent.	
1	25	23	2	10	789	359	31.3	35.9
2	25	21	4	20	588	560	48.7	23.0
3	25	19	6	30	465	683	59.6	22.7
4	25	17	8	40	381	767	66.8	19.2
5	25	15	10	50	325	823	71.7	16.5
6	25	13	12	60	294	854	74.4	14.2
7	25	11	14	70	291	857	74.7	12.2
8	25	9	16	80	254	894	77.8	11.2
9	25	7	18	90	241	907	79.0	10.1
10	25	5	20	100	233	915	79.6	9.2

Protein in blank = 1,148 milligrams.

The digestions at 70° show that the activity in the presence of large amounts of enzyme is not greatly weakened, but with decreasing percentages of gum the loss becomes more marked. The data covering the digestions at various temperatures are plotted in fig. 4. This resistance to heat is rather unusual for an enzyme, but has been commented upon by various investigators of papain. Delezenne, Mouton, and Pozerski<sup>\*</sup> note the rapid action upon egg white and serum at temperatures of 80° and 90°. Chittenden<sup>\*</sup> found that papain in acid solution digests more meat protein at 70° than at lower temperatures. However, I have found that a papain solution rapidly heated to 100°, allowed to boil five seconds, and immediately cooled with ice no longer shows any proteolytic activity.

#### STANDARD EVALUATION OF PAPAIN

An examination of the curves in fig. 1 shows that the percentage of protein digested in thirty minutes increases rapidly with small increments of enzyme in the first portion of the curve. The range between 0.0 and 10 milligrams of papain closely approximates a straight line, especially with ordinary samples of gum, while the ratio of papain to protein digested falls off more or less rapidly beyond this point, depending upon the activity of the enzyme. The percentage of protein digested by amounts smaller than 10 milligrams of low-grade papain is so slight that this weight of gum has been decided upon as the best for routine analyses. It is suggested that the average of 6 determinations carried out in the manner previously described under "methods of analysis," using 25 cubic centimeters of milk, 23 cubic centimeters of distilled water, and 2 cubic centimeters of a filtered solution representing 10 milligrams of papain digested for thirty minutes at 40°, be accepted as the standard and that the proteolytic activity of the gum be designated by the ratio so obtained of 1 part of papain to the digested protein. This may be called the activity number of the sample.

Table XXVIII shows the activity upon this basis of the different samples of papain mentioned in this paper.

<sup>\*</sup> *Compt. rend. Soc. biol.* (1906), 60, 68 and 309; Pozerski, *Ann. Inst. Pasteur* (1909), 23, 205 and 321.

<sup>\*</sup> *Trans. Conn. Acad. Arts & Sci.* (1892), 9, 311.

TABLE XXVIII.—Activity of various samples of papain.

Sample No.	Source.	Activity number.
1	Unknown	0.0
2	Ceylon	0.1
3	do	5.6
4	do	9.6
5	do	5.7
6	do	22.0
7	do	1.8
8	Mexico	12.9
9	West Indies	40.0
10	Fresh latex	45.8
11	Philippine, sundried	45.4
12	Philippine, alcohol precipitation	72.2

## OTHER ENZYMES IN PAPAYA LATEX

Fresh papaya latex was investigated to determine whether enzymes other than papain were present. Flasks containing the following mixtures were incubated for twenty-four hours at 40°. The solutions were made neutral to phenolphthalein before incubation.

## 1. Active control.

Latex	g.	1.0
Water, distilled	cc.	50.0
Toluol	cc.	0.5

## 2. Boiled control.

Latex, boiled 1 minute	g.	1.0
Water, distilled	cc.	50.0
Toluol	cc.	0.5

## 3. Active extract (made in triplicate).

Latex	g.	1.0
Sucrose	g.	0.5
Water, distilled	cc.	50.0
Toluol	cc.	0.5

No invert sugar was produced in any of these experiments thus showing the absence of invertase.

## 4. Active control.

Latex	g.	1.0
Water, distilled	cc.	50.0
Toluol	cc.	0.5

## 5. Boiled control.

Latex, boiled 1 minute	g.	1.0
Water, distilled	cc.	50.0
Toluol	cc.	0.5

## 6. Active extract (made in triplicate).

Latex	g.	1.0
Starch solution, 1 per cent	cc.	50.0
Toluol	cc.	0.5

No reducing sugars were found in any of these experiments, thus showing the absence of diastase in the latex. It is probable that the reported presence of this enzyme in commercial papain is to be attributed to the adulterants used in its preparation.

The fresh latex gave a faint blue with tincture of guaiacum, indicating the presence of traces of oxidase. The color darkens to a very pronounced blue upon the addition of hydrogen peroxide, while a control sample boiled for one minute gave no color. The fresh latex gave no color with *p*-phenylene diamine, but turned deep red at once upon the addition of hydrogen peroxide. Similar results were obtained with Röhmann's reagent (*p*-phenylene diamine and alpha naphthol in sodium carbonate solution).

The fresh latex, therefore, contains considerable amounts of a peroxidase, the presence of which is doubtless responsible for the darkening of color that takes place so readily during drying.

Digestion mixtures, using olive oil or ethyl acetate as the substrate, were incubated for forty-eight hours in the usual manner employed in testing for fat-splitting enzymes. The presence of lipase could not be definitely established, although in some cases a slight increase of acidity indicated the possibility of traces being present.

#### YIELD OF PAPAIN

It is difficult to estimate the amount of papain that may be obtained from papaya trees grown especially for this purpose. There is no doubt but that proper cultivation greatly increases the available supply of latex and that rich free soil produces plants more capable of recuperating from the effects of tapping. Under ordinary conditions such as prevail in Ceylon, a yield of 1 kilogram of fresh latex may be obtained from about 5 trees. Much depends upon the age of the plant and the maturity of the fruit at the time of tapping. Small immature fruits give a meager flow of latex that coagulates immediately, while larger papayas, about two-thirds mature, give a much larger yield and are to be chosen for tapping. The latex from such fruits does not coagulate rapidly, but freely drips into the collecting dish for several minutes following scarification. Two hundred fifty such fruits gave 1 kilogram of fresh latex, representing about 200 grams of well-dried papain. This is a much lower yield than may be obtained under favorable conditions. Forty fruits of medium size averaging about 800 grams in weight yielded 1 kilogram of latex, or 3 per cent. An average

tree in full bearing produces from 40 to 50 fruits during a season.

Subsequent tapplings of the same fruits give a further amount of latex, but the yield in this case is considerably less. The fruits ripen more rapidly after scarification and are injured in appearance, but suffer little if any in flavor. They are not acceptable in the market, but could be utilized in various ways as a by-product where trees are primarily grown for the manufacture of papain.

#### PREPARATION OF PAPAYA

Papaya trees mature rapidly, and suffer little from the attacks of insects or plant diseases. They are generally propagated from the seed, which should be planted in boxes filled with rich earth, the seeds being about 2 centimeters apart each way and at a like depth. The plants grow freely, and may be transplanted at the end of three weeks. They should be placed about 3 to 4 meters apart, well watered, and shaded for a time. If a nursery is used, the plants may be set out from 20 to 30 centimeters apart in rows at intervals of 1 meter. The young plants should preferably be transplanted before reaching a height of over 30 centimeters. Some of the seedlings will be males, and the majority of these should be replaced by either females or bisexual plants. The trees may be depended upon to blossom and produce fruit within a year, but the number and size of the fruits will not reach a maximum until the following season. Tapping may be carried out during the second year and thereafter, until the trees become unprofitable due to age and the decreasing size of the papayas. When the trees become so tall that the latex is difficult to gather, the trunk may be cut off at a height of about 1 meter from the ground. Buds will form from the stump and produce new branches, all of which except 2 or 3 should be removed; otherwise, the fruits will be small. It has been reported that these shoots grow readily when planted, and if this is found to be the case it would probably be the best method for propagation. Seeds for planting should be saved only from the best oblong fruits that have never been tapped and have ripened on the tree.

Papaya trees are injured by water standing around the roots, and flourish best in well-drained localities. Excess water and strong winds are the principal factors causing failure, and situations should be chosen where these conditions will not be encountered. If care is taken in collecting the latex to insure freedom from foreign material and the fresh juice is dried

promptly before decomposition sets in, there should be no difficulty in preparing a white papain that would find a ready sale. Drug firms at present are at the mercy of the market, and frequently cannot obtain satisfactory papain. The enzyme should be sold under a guarantee covering its activity, thus establishing a standard which would command better prices than at present offered and avoid competition with adulterated products.

Letters from various large firms clearly show a willingness to purchase high-quality papain in relatively large quantities, single shipments ranging from 100 to 300 kilograms representing ordinary requests. It must be remembered, however, that the market is limited and, although gradually increasing, that overproduction is always a possibility. The material must be free from impurities, as nearly white as possible, thoroughly dry, and shipped in sealed containers, and must possess the requisite proteolytic activity.

The possibility of establishing a papain industry in the Philippine Islands should receive attention, as it does not necessitate a large investment of capital, and the time required is short before returns may be expected.

## ILLUSTRATIONS

### PLATE I

- FIG. 1. Native of Ceylon with basket made from a leaf sheath of the areca palm for collecting papaya latex. (Photograph by D. S. Pratt.)  
2. Showing method of placing support and hanging basket on the tree. (Photograph by D. S. Pratt.)

### PLATE II

Papain samples, illustrating various grades. (Numbers correspond to text.) (Photograph by Martin.)

- FIG. 1. From local drug store.  
2. Ceylon, grade 2.  
3. Ceylon, grade 1.  
6. Ceylon, from Mead Johnson & Co.  
7. Ceylon, from Mead Johnson & Co.  
8. Mexican, from Mead Johnson & Co.  
9. West Indian, from Mead Johnson & Co.  
10. Philippine, prepared by the author.

### TEXT FIGURES

- FIG. 1. *Curve* 1. Papain from local drug store.  
*Curve* 3. Ceylon papain, sample 3.  
*Curve* 4. Ceylon papain, sample 4.  
*Curve* 5. Ceylon papain, sample 5.  
*Curve* 6. Ceylon papain, sample 6.  
*Curve* 7. Ceylon papain, sample 7.  
*Curve* 8. Mexican papain, sample 8.  
*Curve* 9. West Indian papain, sample 9.  
*Curve* 10. Fresh papaya latex, sample 10.  
*Curve* 12. Papain by alcohol precipitation, sample 12.  
2. Rate of digestion of milk protein by papain.  
3. Digestion in hydrochloric acid solution.  
*Curve* 1. With 50 milligrams of papain.  
*Curve* 2. With 25 milligrams of papain.  
4. Digestions at temperatures from 0° to 70°.



Fig. 1. Native of Ceylon with basket made from a leaf sheath of the areca palm.



Fig. 2. Showing method of placing support and hanging basket on the tree.

PLATE I. COLLECTING PAPAYA LATEX.



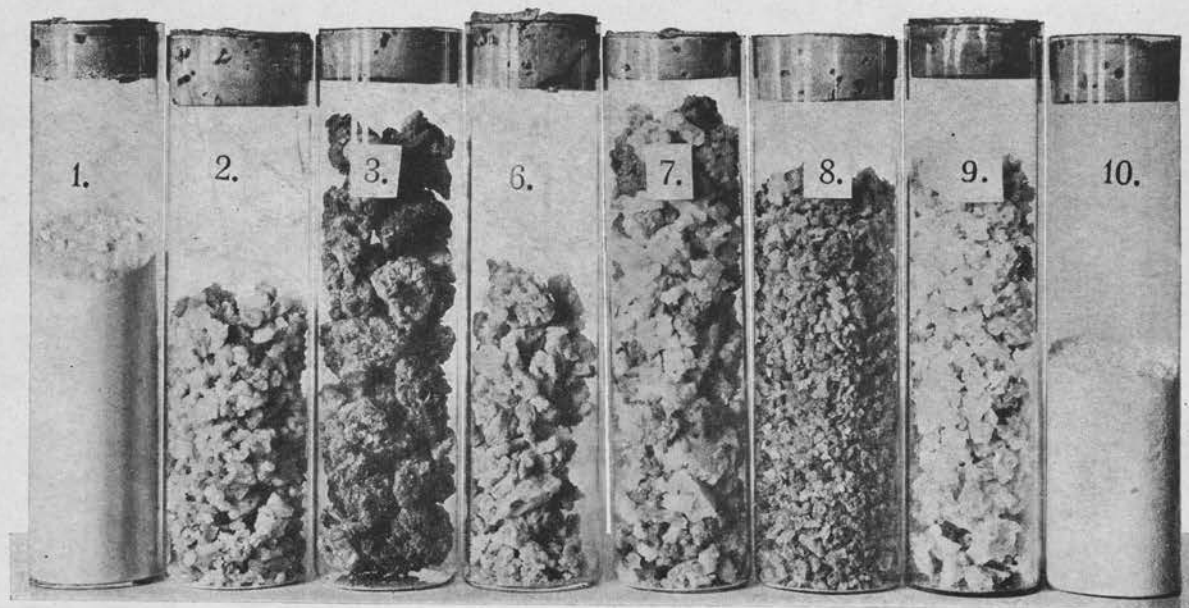


PLATE II. PAPAIN SAMPLES, ILLUSTRATING VARIOUS GRADES.

✓ A DETERMINATION OF THE DIURNAL VARIATION OF THE  
RADIOACTIVITY OF THE ATMOSPHERE AT MANILA  
BY THE ACTIVE DEPOSIT METHOD<sup>1</sup>

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FIVE TEXT FIGURES

Elster and Geitel<sup>2</sup> first discovered that when a negatively charged wire is exposed in the open air it becomes coated with an active deposit which may be detected by the ionization produced when the wire is placed in the ionization chamber of an electroscope. Bumstead<sup>3</sup> showed that the collected mass is a mixture of the active deposits of radium and thorium, and it is generally agreed that its sources are the radioactive substances in the earth. Many observers have attempted to determine the amount of emanation per cubic meter of the atmosphere by measuring the ionization produced by the active deposit collected on a given length of wire at a certain voltage and exposed for a definite period of time. Eve<sup>4</sup> compared the amount of active deposit collected by a wire exposed in the open air with the amount collected by a wire in a closed tank containing the decay products from a known quantity of radium bromide; and, assuming, on experimental evidence, that the wire charged to 10,000 volts collected all the active deposit from a cylindrical space 40 centimeters in radius concentric with the wire, calculated that the deposit per cubic kilometer at Montreal was in equilibrium with 0.14 to 0.49 gram of radium bromide. This is of the same order of magnitude as the amount afterwards found by Eve<sup>4</sup> and others by the charcoal absorption method.

The active deposit method, owing to its simplicity and to the fact that it is the only one yet devised for the detection of

<sup>1</sup> This work has been carried on with the encouragement of Dr. J. R. Wright, who has assisted with many valuable suggestions.

<sup>2</sup> *Phys. Zeitschr.* (1901), 2, 590.

<sup>3</sup> *Am. Journ. Sci.* (1904), IV, 18, 1-11.

<sup>4</sup> *Phil. Mag.* (1905), 10, 98-112.

<sup>5</sup> *Ibid.* (1907), 14, 724.

thorium-decay products in the open air, has been of great utility in the examination of the radioactivity of the atmosphere. Nevertheless, its adequacy for the absolute determination of the amount of emanation present is questionable, for the amount of active deposit collected by a charged wire undoubtedly depends upon other factors in addition to the amount of emanation present. Rutherford<sup>a</sup> states:

It has generally been supposed that only the positively charged atoms of radium A are collected on the wire, and that they travel in an electric field at the same rate as the positive ions. Account has to be taken of the rate of re-combination of the charged atoms of radium A with the negative ions of the air, for only those atoms reach the wire which retain their charge. The constant of re-combination is no doubt affected by atmospheric conditions, and the number of nuclei present.

At high elevations the air, owing to its reduced density, should cause a smaller resistance to the motion of the charged particles, so they should be swept in more rapidly and from a greater distance than at a lower level. Therefore, the amount of active deposit collected should increase with altitude even if the emanation remained constant. Saake<sup>7</sup> found that the active deposit at Arosa, elevation 1,800 meters, was three times as great as that of Wolfenbüttel. Other observers have obtained similar results. That this is not due to an increase in the emanation content is indicated by the determinations of Wright and Smith,<sup>8</sup> who made an investigation of the variation of the radium emanation with altitude by the charcoal absorption method and found that the emanation content at Manila, sea level, was approximately four times that obtained on Mount Pauai, elevation 2,460 meters.

Many observers have found that, for a given locality, the amount of deposit collected depends upon the direction of the wind, but there has been considerable disagreement as to the effect of the variation of the wind velocity. Kinoshita, S. Nishikawa, and S. Ono<sup>9</sup> deduced the lines of flow of the charged particles for different wind velocities from theoretical considerations, and found that, above a critical velocity, the variation should not affect the amount collected.

The diurnal variation of the active deposit has been the subject

<sup>a</sup> Radioactive substances and their radiations. Cambridge University Press (1913).

<sup>7</sup> *Phys. Zeitschr.* (1903), 4, 426.

<sup>8</sup> *This Journal, Sec. A* (1914), 9, 51.

<sup>9</sup> *Phil. Mag.* (1911), 22, 821.

of a very limited amount of investigation. It was first detected by Simpson,<sup>10</sup> who made three determinations per day in Lapland for several months and found that there was a maximum in the morning and a minimum in the afternoon. Hess<sup>11</sup> also found a small variation with a minimum in the evening. Neither of these observers made observations covering the entire twenty-four hours. Dike<sup>12</sup> secured the active deposit by forcing a measured stream of air past charged screens. His mean curve for six series of observations, each set of observation extending over a period of about twenty hours, shows a striking variation. The maximum comes soon after midnight, and is more than twenty times the minimum.

In the present investigation the meteorological data were secured from the Manila Observatory, which is about 0.1 kilometer from the point where the measurements were made. The method was similar to that commonly used in active deposit observations. The testing apparatus was a standard Exner electroscope. The hollow, brass supporting neck was filled with sulphur which supported a central rod and a guard ring, the latter was kept charged to 240 volts by means of a storage battery in order to reduce the natural leak. The upper end of the central rod supported the gold leaf, while the end entering the ionizing chamber was rigidly attached to a wire cage 9 centimeters in diameter and 17 centimeters high. The ionizing chamber was of sheet brass, 22 centimeters in diameter and 24 centimeters deep. A saturation test of the apparatus showed that for the voltage used in the determinations more than 85 per cent of the negative ions reached the charged system. The capacity of the system was about 18 electrostatic units. The motion of the leaf was observed by means of a telescope having a micrometer eyepiece. The electroscope had a sensitiveness of approximately 5 divisions per volt. A bare wire was wound on an iron reel fitting snugly into the ionizing chamber. After the introduction of the reel, the bottom of the chamber was closed, the leaf charged to 240 volts, and the motion of the leaf in divisions per minute recorded as the natural leak. The wire was then stretched horizontally, by means of ebonite rods, at a mean elevation of 3 meters, in the open space north of the physics building. Since no static machine was at first avail-

<sup>10</sup> *Phil. Trans. Roy. Soc. London* (1905), A, 205, 61.

<sup>11</sup> *Sitzungsber. Akad. d. Wiss., math.-nat. Klasse*, Wien (1910), 119, 145.

<sup>12</sup> *Terr. Mag.* 1906), 7, 125.

able, the wire was charged by a metal comb which was brought near to another comb fastened to the negative terminal of a Thordarsen induction coil capable of giving a 20-centimeter spark. The silent leak across the air gap was usually sufficient to keep the deflection of a Braun electrostatic voltmeter constant at about 3,000 volts. After midnight, however, the humidity was so great that the potential could not be maintained, so a motor-driven static machine was substituted for the induction coil, the aerial being connected directly to the negative terminal. With this the potential was kept at 8,000 volts, the pressure being regulated by varying the distance between two combs, one of which was in contact with the wire, while the other was grounded. After the wire had been exposed for thirty minutes, it was wound on the reel and introduced into the ionizing chamber. After ten minutes the leaf was charged to 240 volts by means of storage cells, and the time for it to move 40 divisions was recorded as the reciprocal of the amount of active deposit on the wire.

*Amount of active deposit at Manila.*—Elster and Geitel<sup>13</sup> took as a measure of the amount of active deposit present the leak per hour in volts which would be caused by the active deposit collected by a wire 1 meter long which had been exposed for two hours at a negative voltage of 2,500, the testing system having a capacity of 9.5. The capacity of my electroscope was about 18 electrostatic units, otherwise the experiments were carried on in the same manner. A wire 30 meters long exposed at Manila gave a mean discharge for 5 observations of 300 volts per minute. If the capacity of my electroscope had been 9.5, as in the case of the Elster and Geitel experiment, the discharge would have been about 568 volts per minute. Therefore, a wire 1 meter long would give a discharge of about 19. This is approximately the same as the mean value found by Elster and Geitel for Wolfenbüttel.

*Diurnal variation of the active deposit.*—The diurnal variation was determined as follows: The wire was exposed at 8,000 volts for a period of thirty minutes. It was then tested as described above, and the time for the leaf to move 40 divisions was recorded as the reciprocal measure of the amount of active deposit collected. The actual determinations are given in Table I.

<sup>13</sup> *Phys. Zeitschr.* (1903), 4, 526.

TABLE I.—Diurnal variation of active deposit.

[Length of wire, 80 meters; voltage, 8,000; time of exposure, 30 minutes.]

Date.	Time af- ter mid- night.	Recipro- cal of time for leaf to move 40 divisions.	Wind.		
			Relative humidity.	Dirrec- tion.	Force in kilo- meters per hour.
1914.	Hrs.				
Jan. 26	10	0.028			
Jan. 27	19	0.008			
Jan. 28	21	0.018			
Do	24	0.050			
Jan. 29	3	0.143			
Do	5	0.121			
Do	6½	0.033			
Do	9	0.033			
Do	11½	0.022			
Do	15	0.016			
Do	17	0.018			
Do	20½	0.019			
Feb. 2	20½	0.018	76	ESE	8½
Feb. 3	1	0.014	83	Calm	2
Do	2	0.012	86	Calm	0
Do	3	0.033	86	Calm	1
Do	4	0.121	88	Calm	1
Do	5	0.091	86	Calm	½
Do	6½	0.025	92	Calm	3
Do	9½	0.020	79	SSW	3½
Do	11½	0.023	72	SW	9
Do	13	0.050	68	SE	8
Do	19	0.007		Calm	
Feb. 4	20	0.033	82	Calm	2
Feb. 5	1	0.023	89	Calm	3
Do	2	0.050	83	E	6
Do	3	0.062	91	NE	4
Do	3½	0.100	91	NE	4
Do	5	0.050	93	Calm	3
Do	6	0.036	93	Calm	2½
Do	9	0.030	68	ESE	16
Do	12	0.033	55	EbyS	22
Do	16	0.026	48	ESE	20
Do	18½	0.009	58	ESE	16
Do	20½	0.013			
Feb. 9	21	0.015	74	ESE	8
Do	24	0.030	84	Calm	1½
Feb. 10	3	0.125	77	Calm	1½
Do	7½	0.025	80	Calm	0
Do	8½	0.017	62	NE	12½
Do	11½	0.017	58	NE	9½
Do	14½	0.014	69	Calm	1½
Do	16½	0.015	63	NNE	11
Feb. 15	8	0.008	66	Calm	3
Do	9	0.025	55	EbyS	4½
Do	12	0.017	55	W	17
Do	14	0.011	46	W	10

TABLE I.—Diurnal variation of active deposit—Continued.

Date.	Time after mid-night.	Reciprocal of time for leaf to move 40 divisions.	Relative humidity.	Wind.	
				Direction.	Force in kilometers per hour.
1914.	Hrs.				
Feb. 16.....	16	0.008	47	SE	22
Do.....	20½	0.020	58	ESE	10
Do.....	24	0.045	79	ESE	8
Feb. 17.....	3½	0.076	87	NNE	4½
Do.....	7	0.033	89	NE	4½
Mar. 9.....	15	0.009	44	SE	27
Do.....	17	0.009	57	SE	18
Do.....	21	0.011	78	SE	7
Do.....	23½	0.050	84	ESE	6
Mar. 10.....	1	0.040	87	Calm	3
Do.....	3	0.033	94	E	1
Do.....	5	0.033	93	ENE	3
Do.....	6	0.018	91	Calm	4
Do.....	9½	0.020	61	Calm	2½
Do.....	13	0.075			
Mar. 18.....	13½	0.010	58	SSE	1
Do.....	17	0.008	57	SE	14
Do.....	20	0.009	67	SE	5
Do.....	22½	0.025	73	E	6
Do.....	24	0.020	82	Calm	2
Mar. 19.....	1½	0.025	79	E	6
Do.....	2	0.033	83	Calm	1
Do.....	3	0.014	80	Calm	2
Do.....	4	0.025	83	Calm	1
Do.....	5	0.026	85	Calm	½
Do.....	6½	0.028	89	Calm	1½
Do.....	9	0.024	66	W	9
Do.....	11½	0.014	66	WNW	15
Do.....	12½	0.010	59	WNW	14½
Mar. 24.....	20½	0.006	67	SE	8
Do.....	24	0.047	73	NE	11
Mar. 25.....	3	0.050	80	Calm	2½
Do.....	4	0.052	84	Calm	0
Do.....	8½	0.022	65	ENE	3
Do.....	10½	0.017	67	W	5
Do.....	11½	0.020	59	W	14
Do.....	15½	0.005	37	SE	23
Do.....	17	0.012	36	ESE	18
Mar. 30.....	10	0.022	61	SSW	4
Do.....	13½	0.012	56	W	15
Do.....	16½	0.010	45	SE	7
Do.....	22½	0.010	76	SSE	9
Mar. 31.....	2	0.025	83	Calm	0
Do.....	5	0.050	83	Calm	0
Do.....	7	0.012	77	Calm	0
Do.....	8½	0.015	69	Calm	1
May 4.....	21½	0.020	62	ESE	7
Do.....	22½	0.030	70	SE	8

TABLE I.—Diurnal variation of active deposit—Continued.

Date.	Time af- ter mid- night.	Recipro- cal of time for leaf to move 40 divisions.	Relative humidity.	Wind.	
				Dirrec- tion.	Force in kilo- meters per hour.
1914.	<i>Hrs.</i>				
May 4 .....	23½	0.063	73	SE	6
May 5 .....	½	0.029	79	Calm	2
Do .....	1½	0.040	81	Calm	3
Do .....	2½	0.040	80	Calm	3
Do .....	3½	0.050	80	Calm	3
Do .....	4½	0.055	83	Calm	1
Do .....	6	0.033	80	Calm	2
Do .....	10½	0.025	70	WNW	10
Do .....	11½	0.015	72	WNW	16
Do .....	15	0.012	48	SE	17
Do .....	19½	0.008	68	ESE	7

The wind, humidity, and active deposit were plotted as ordinates with the times after midnight as the abscissæ. The collection on windy days did not differ noticeably from those taken in times of calm, and variations of the wind were not accompanied by corresponding fluctuations in the deposit (fig. 5); so, apparently, variation of the wind velocity does not affect the amount of active deposit collected. All the active deposit curves show minima in the evening and maxima after midnight. The depression shown in Dike's curve for early morning is lacking in all of my observations. From the mean curves (figs. 2, 3, 4) it will be seen that there are corresponding variations in the humidity and deposit, but the individual curves show that minor variations of the humidity are not usually accompanied by variations of the deposit, which indicates the existence of other factors (fig. 5). One of these factors is the variation in the emanation content, since Wright and Smith<sup>14</sup> have found that the night emanation content at Manila, as measured by the charcoal absorption method, is about twice that of the day.

#### DIURNAL VARIATION AT A HIGH ELEVATION

Observations of the active deposit were made on Mount Maquiling, 60 kilometers from Manila, at an elevation of about 1,140 meters. The apparatus was similar to that used at Manila except that the guard ring was eliminated. The electroscope

<sup>14</sup> *This Journal, Sec. A (1914), 9, 68.*



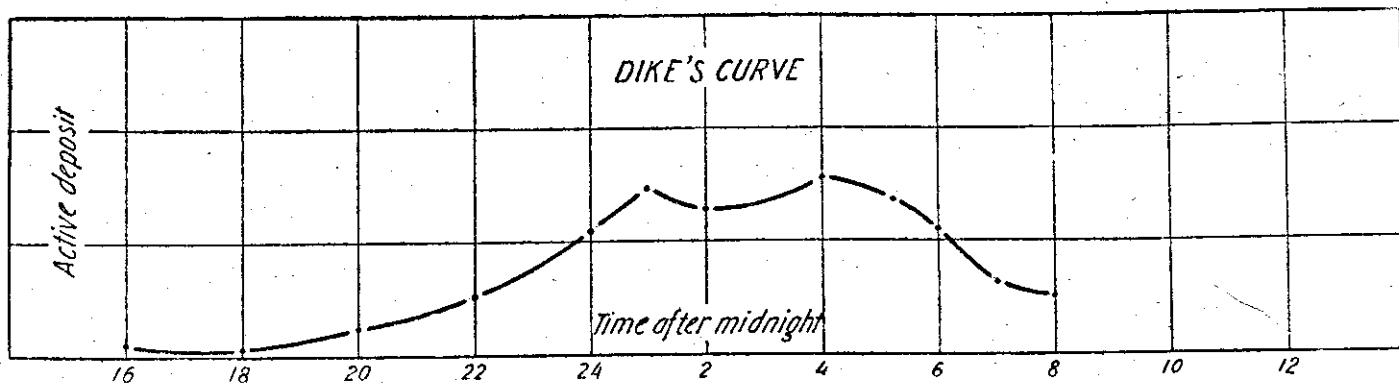


FIG. 1. Active deposit curve.

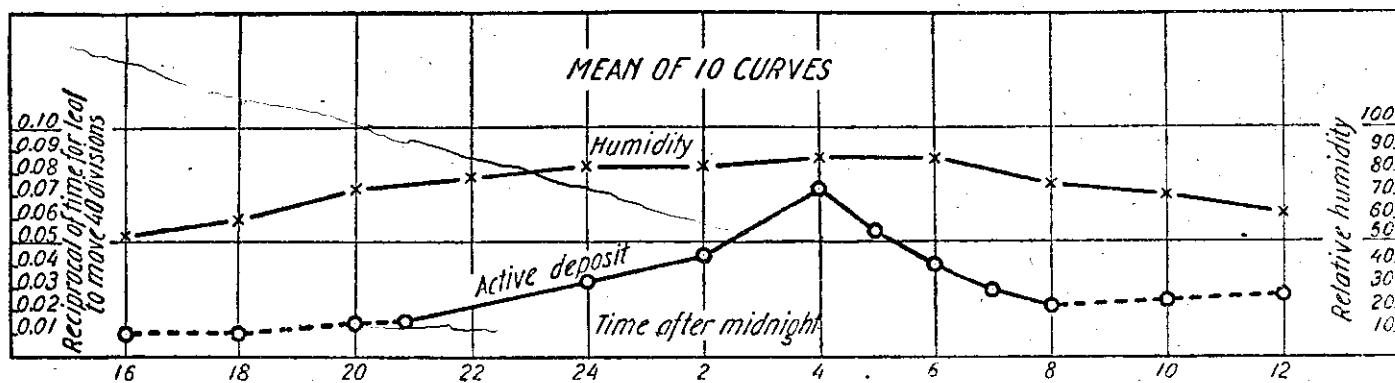


FIG. 2. Active deposit and humidity curves.

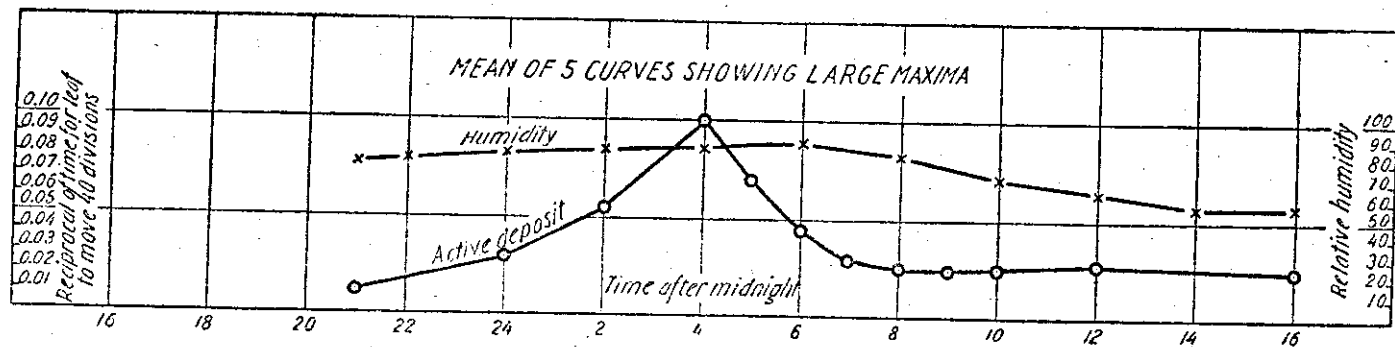


FIG. 3. Active deposit and humidity curves.

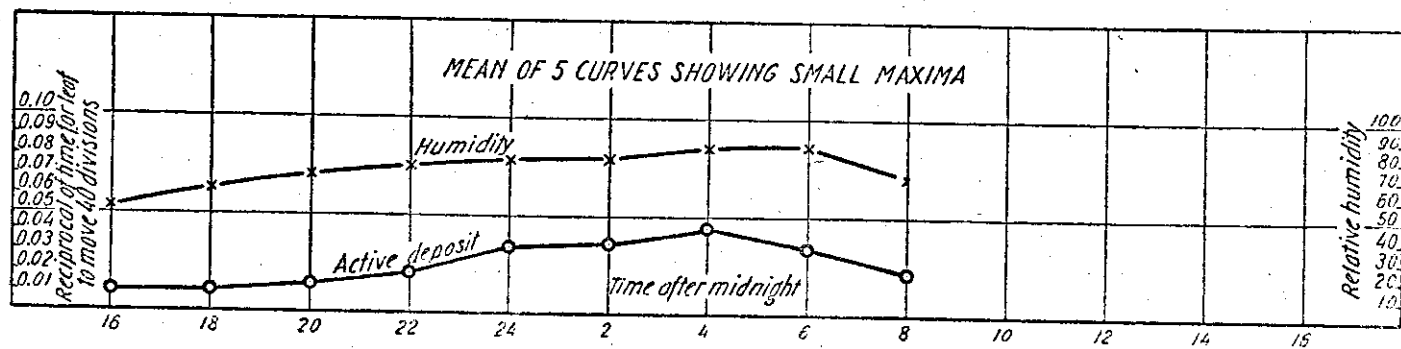


FIG. 4. Active deposit and humidity curves.

was charged by means of an ebonite rod. The humidity, as shown by a self-registering hygrometer, remained above 90 per cent even at midday, and at night it was found necessary to heat the ebonite rods in order to maintain the voltage. The number of determinations is hardly sufficient to justify definite conclusions, but the night determinations are all smaller than the mean-day collection, and apparently the diurnal variation is the inverse of that at Manila. Five daytime determinations made at Manila with the apparatus as used on the mountain gave a

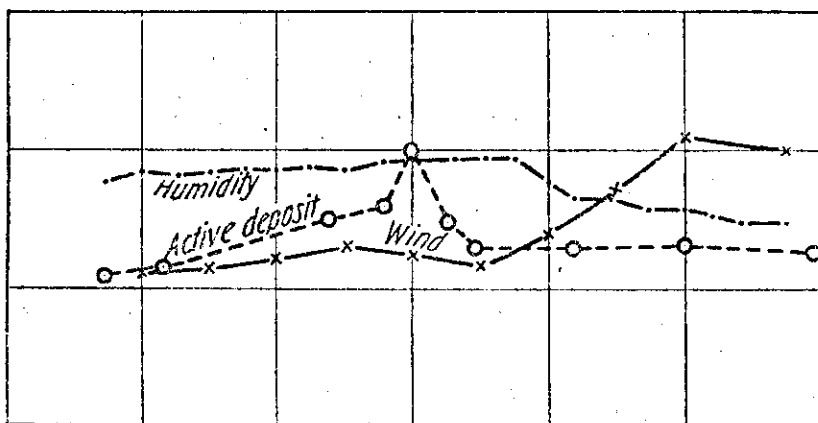


FIG. 5. Humidity, active deposit, and wind curves for February 4, 1914.

mean value for the active deposit approximately one-half that of Mount Maquiling.

*Ratio of the amount of radium active deposit to thorium active deposit at Manila.*—A wire was exposed as outlined above, and the voltage was kept at 10,000 for ninety minutes. The discharge was measured every three minutes after the introduction of the cage into the ionizing chamber and the ionization curve plotted. Thirteen closely agreeing determinations were made, and the mean time required for the rate of discharge to fall to one-half was found to be sixty-two minutes. According to the determination of Harvey,<sup>15</sup> this corresponds to less than 15 per cent thorium active deposit.

<sup>15</sup> *Phys. Rev.* (1912), 35, 9123.

TABLE II.—*Diurnal variation of the active deposit collected on Mount Maquiling, Laguna Province, Luzon.*

Date.	Time after mid-night.	Reciprocal of time for leaf to move 40 divisions.
1914.	Hrs.	
May 16.....	8½	0.017
Do.....	10	0.017
Do.....	12	0.014
Do.....	14	0.008
Do.....	17½	0.010
Do.....	22	0.008
May 17.....	3	0.008
Do.....	7	0.012
Do.....	9½	0.029
Do.....	13½	0.017
Do.....	16½	0.040
Do.....	19	0.021
May 18.....	1	0.005
Do.....	6½	0.005
Do.....	9	0.008
Do.....	12	0.012
Do.....	14½	0.022
Do.....	18	0.014
Do.....	21	0.004
May 19.....	7½	0.008
Mean day value.....		0.007
Mean night value.....		0.09

## SUMMARY

1. The mean day-value of the active deposit at Manila is about the same as that of Wolfenbüttel.

2. (a) There is a large and fairly regular diurnal variation of the active deposit at Manila, the mean night-value being about three times that of the day. (b) The mean active deposit seems to vary with the humidity, but in the individual curves there are wide divergences. (c) There is no evident relation between the wind and the amount of deposit collected.

3. (a) The active deposit collected on Mount Maquiling, elevation 1,140 meters, is about twice that of Manila. (b) The diurnal variation on the mountain is apparently the inverse of that of Manila, the night collection being smaller than the day.

4. The half-period value found at Manila is about sixty-two minutes, which corresponds to less than 15 per cent thorium active deposit.

## ILLUSTRATIONS

### TEXT FIGURES

- FIG. 1. Active deposit curve.  
2. Active deposit and humidity curves.  
3. Active deposit and humidity curves.  
4. Active deposit and humidity curves.  
5. Humidity, active deposit, and wind curves for February 4, 1914.

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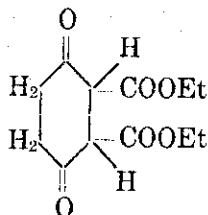
DIETHYLSUCCINOSUCCINATE  
(ETHYLDIOXYDIHYDROTERAPHTHALATE):  
A STUDY OF ITS CONSTITUTION, SOME DERIVATIVES, AND  
ABSORPTION SPECTRA<sup>1</sup>

By H. D. GIBBS and H. C. BRILL

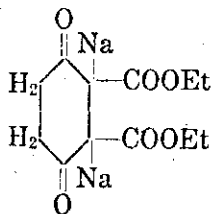
(From the Laboratory of Organic Chemistry, Bureau of Science,  
Manila, P. I.)

THREE TEXT FIGURES

Fehling<sup>2</sup> first produced dimethylsuccinosuccinate in the course of his studies on the action of alkali metals upon methysuccinate. The work of F. Herrmann<sup>3</sup> added greatly to the knowledge of the structure of this compound. He gives formulas to show its relation to phthalic acid in the sense of the formula



and for the sodium salt he gives the formula



in both of which the carboxyl groups are in the ortho position.

Düisberg<sup>4</sup> pointed out the fact that neither the above formula nor the formula in which the carboxyl groups are in the para position was proven.

The work of Geuther,<sup>5</sup> Wedel,<sup>6</sup> and Ebert<sup>7</sup> also contributed

<sup>1</sup> Received for publication August 18, 1914.

<sup>2</sup> *Ann. d. chem.* (1844), 49, 192.

<sup>3</sup> *Ann. d. chem.* (Liebig) (1882), 211, 306.

<sup>4</sup> *Ber. d. deutschen chem. Ges.* (1883), 16, 138.

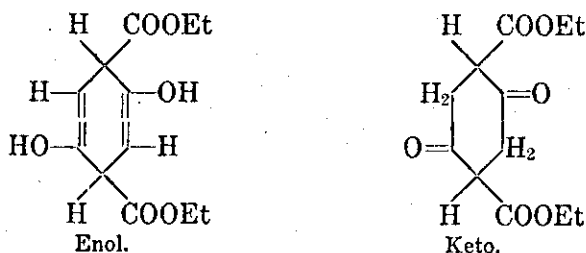
<sup>5</sup> *Ann. d. chem.* (1883), 219, 119.

<sup>6</sup> *Ibid.* (1883), 219, 71.

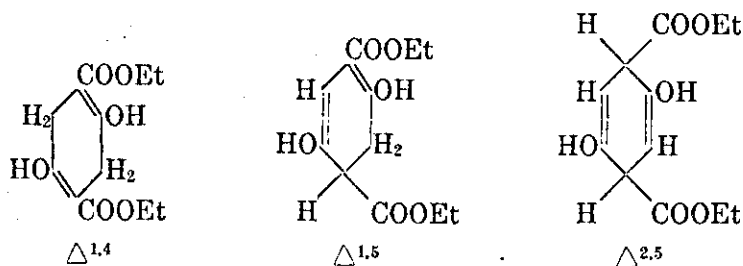
<sup>7</sup> *Ibid.* (1885), 229, 45.

to the knowledge of the structure of the compound. The latter discussed the probability of the carboxyl group being in the para position.

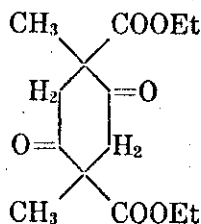
Baeyer<sup>8</sup> showed the relationship to terephthalic acid and that the compound must exist in the two forms



The latter conclusion was based upon the fact that phenylhydrazine, ammonia, and hydroxylamine react as if the compound were in the keto form, while the reaction with acetyl chloride (forming a diacetate) and the salt formation with alkalis indicated the enol form. He also shows that the three representations



are possible for the enol form.<sup>9</sup> He later prepared the derivative



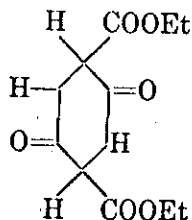
by treating the sodium compound of ethylsuccinosuccinate with methyl iodide. This compound yields a mono- and a diphenylhydrazone, as would be expected from the above representation, in the same manner as does ethylsuccinosuccinate itself.

<sup>8</sup> *Ber. d. deutschen chem. Ges.* (1886), 19, 428 and 1799. See also Baeyer and Tutein, *Ibid.* (1889), 22, 2189.

<sup>9</sup> *Ann. d. chem.* (1888), 245, 190.

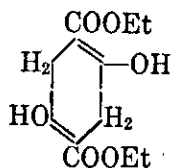
The existence of mixed crystal forms in ethylsuccinosuccinate and diethylquinonedihydroparacarboxylate was discovered by Lehmann and discussed by Herrmann.<sup>10</sup> The possibility of the existence of desmotropic forms and derivatives has been discussed by Hantzsch and Herrmann.<sup>11</sup>

Hantzsch<sup>12</sup> refers to the oxidation of ethylsuccinosuccinate as producing quinonedihydroterephthalic ester of the constitution



which may indicate that the 3,6 hydrogen atoms of ethylsuccinosuccinate are the first to be oxidized.

From the work described in this paper we believe that ethylsuccinosuccinate can exist in two forms, the enol and keto, *cis* and *trans* modifications being also possible; it seems reasonable to assume that one of these in the keto compound will favor the migration to the enol form. Of the three forms which Baeyer shows are possible for the enol modification the  $\Delta^{1,4}$



is the only one tenable when the labile hydrogen atoms are in the 1,4 positions, which from the evidence at hand, seems to be the case.

#### ENOL AND KETO FORMS

When the mother liquor from which a considerable quantity of ethylsuccinosuccinate has been obtained is concentrated, a small amount of a yellow crystalline precipitate is thrown out. The purification of this compound was effected by crystallizing many times from absolute alcohol. The specimen thus obtained differs from the first precipitate formed in color, melting point, solubility, and absorption spectra and shows some differences in chemical behavior.

<sup>10</sup> *Ber. d. deutschen chem. Ges.* (1886), 19, 2235.

<sup>11</sup> *Ibid.* (1887), 20, 2801.

<sup>12</sup> *Ibid.* (1886), 19, 26.



The first compound thrown out is very slightly colored greenish yellow, melts at  $127^{\circ}$ , is less soluble in alcohol, the absorption band is less persistent, and the compound absorbs bromine in alcoholic solution and gives an initial pink color with sodium ethoxide. The second precipitate formed is yellow, melts at  $123^{\circ}$ , is slightly more soluble, its absorption band is the more persistent, does not absorb bromine, and gives an initial red color with sodium ethoxide.

The two specimens were treated in cold alcoholic solution with alcoholic bromine solution by the method of Kurt H. Meyer<sup>13</sup> to determine the percentage of enol and keto forms. The light-colored samples were shown by the average of a number of titrations to be approximately 90 per cent enol, while the yellow specimen reacted only to a very slight extent with the bromine solution (1 or 2 drops producing a bromine color), showing it to be practically all in the keto form. (The calculation is based upon the addition of 4 atoms of bromine to 1 atom of the ester.)

This behavior of the compound was noted by F. Herrmann,<sup>14</sup> while preparing a bromine addition product of ethylsuccinosuccinate. His preparations would not absorb the theoretical amount of bromine and he states that the yellow color obtained at the end of the titration was not necessarily due to free bromine but to decomposition products. In the light of our present knowledge we believe the yellow color of the solution, after complete bromine absorption, to be due to the keto form which has been unacted upon.

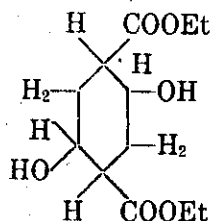
#### REDUCTION OF ETHYLSUCCINOSUCCINATE

On treating an alcoholic solution of ethylsuccinosuccinate (90 per cent enol form) with a small quantity of concentrated hydrochloric acid and adding zinc dust in small amounts a colorless crystalline substance is thrown out of the solution. This compound is practically insoluble in alcohol and water, but is soluble in warm toluene from which it can be thrown out in beautiful colorless crystals by the addition of alcohol; melting point,  $120^{\circ}$ . It is soluble in alkalies, forming a solution which quickly turns brown in the air. On treatment with acetyl chloride a derivative is formed which melts at  $167^{\circ}$ , 2 degrees below the melting point of the diacetyl derivative of ethylsuccinosuccinate. It becomes yellow on heating, while the diacetyl derivative of

<sup>13</sup> *Ann. d. chem.* (1911), 380, 212.

<sup>14</sup> *Ber. d. deutschen chem. Ges.* (1886), 19, 2229.

ethylsuccinosuccinate does not. Mixtures of the two compounds melt at 166°. It is possible that this is the reduced ethylsuccinosuccinate of the following constitution:



The absorption spectrum shows some differences from the known diacetyl derivative. It was observed that the crystals of diethylsuccinosuccinate which form on cooling the filtrate obtained after the reduction with zinc dust and hydrochloric acid are more yellow than the original compound employed. This may indicate that the enol form is more readily reduced, the keto form remaining in a greater proportion than was originally present.

**Absorption spectra.**—The absorption spectra of two samples of ethylsuccinosuccinate, one 90 per cent enol melting at 127° and the other practically all keto melting at 123°, in neutral alcohol solution and with 2 equivalents of sodium ethoxide, and the diacetate of ethylsuccinosuccinate are plotted in fig. 1.

It is to be noted that the absorption band heading at  $1/\lambda = 2,660$  in neutral solution is more persistent in the keto form, while in alkaline solution the reverse is the case. This points to the conclusion that the color is due to the keto form and that this compound is less affected by alkalies. The curve of the acetyl derivative shows no absorption band and leads to the conclusion that the labile hydrogen of the hydroxyl is necessary to selective absorption. The shift of the band produced by sodium ethoxide is found in all hydroxy benzene derivations examined.<sup>15</sup>

The absorption curve of the diimide<sup>16</sup> of ethylsuccinosuccinate in neutral solution and in the presence of an excess of hydrochloric acid are plotted in fig. 2.

Since this compound is a derivative of the keto form in which the oxygen atoms are replaced by the more active =NH groups, it is to be expected that it will be more highly colored than the keto ethylsuccinosuccinate and show a greater absorption band in the same region of the spectrum. Acids form salts with this

<sup>15</sup> Gibbs and Pratt, *This Journal*, Sec A (1913), 8, 33.

<sup>16</sup> Baeyer, *Ber. d. deutschen chem. Ges.* (1886), 19, 429.

compound and saturate the free affinities of the nitrogen atom destroying the band.

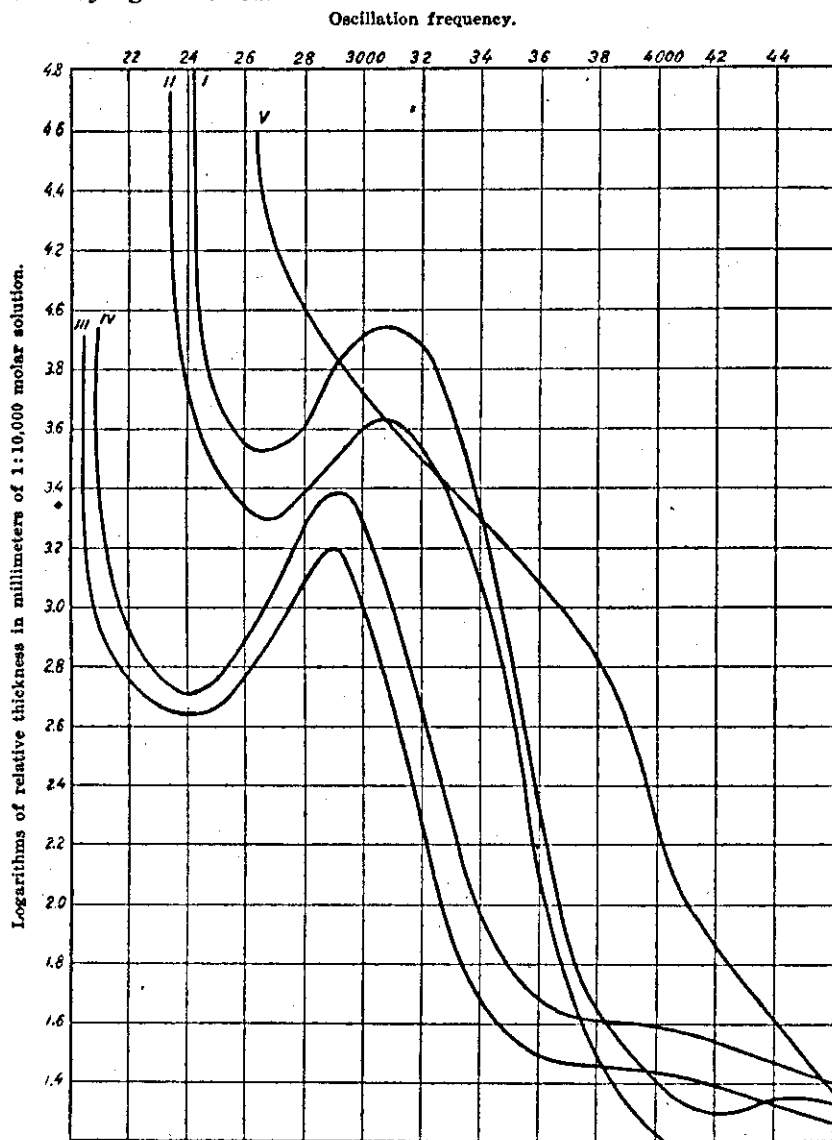


FIG. 1. Curve I. Diethylsuccinosuccinate in alcohol. Light yellow modification. Curve II. Diethylsuccinosuccinate in alcohol. Deep yellow modification. Curve III. Diethylsuccinosuccinate in alcohol plus 2 equivalents of sodium ethylate. Light yellow modification. Curve IV. Diethylsuccinosuccinate in alcohol plus 2 equivalents of sodium ethylate. Deep yellow modification. Curve V. Diacetyldiethylsuccinosuccinate in alcohol.

The absorption curves of methylsalicylate in neutral alcohol and in the presence of a great excess of sodium ethoxide and of the acetyl derivative of methylsalicylate are plotted in fig. 3.

The great difference in the curve of the acetyl derivative from those of the first two compounds, shows that the fixation of the labile hydrogen atom has the same general effect as in ethylsuccinosuccinate and its diacetyl derivative. In the latter the spectrum shows only general absorption since the benzene ring

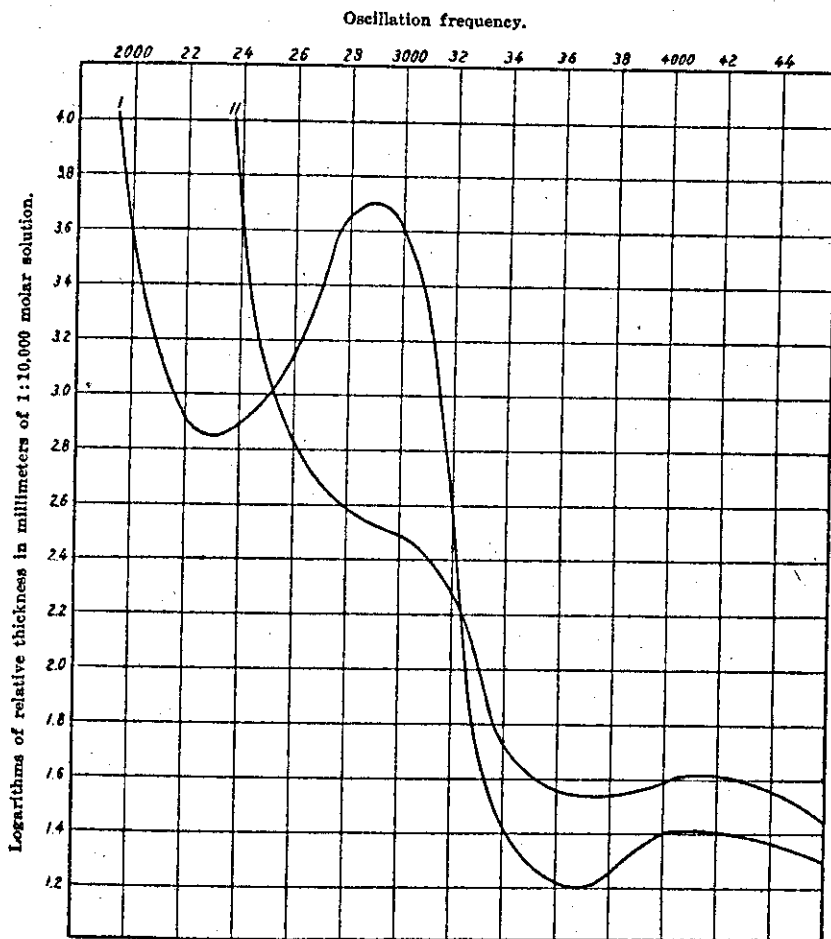


FIG 2. Curve I. P-dilimide of diethylsuccinosuccinate in alcohol. Curve II. P-dilimide of diethylsuccinosuccinate in alcohol plus 2 equivalents of hydrochloric acid.

is more nearly saturated. The entire disappearance of an absorption band in acetylmethylsalicylate is not to be expected since phthalic acid<sup>17</sup> and phthalic anhydride show a similar absorption band due to the effect of the vibration of the benzene ring.

<sup>17</sup> Pratt, *This Journal*, Sec. A (1913), 8, 399.

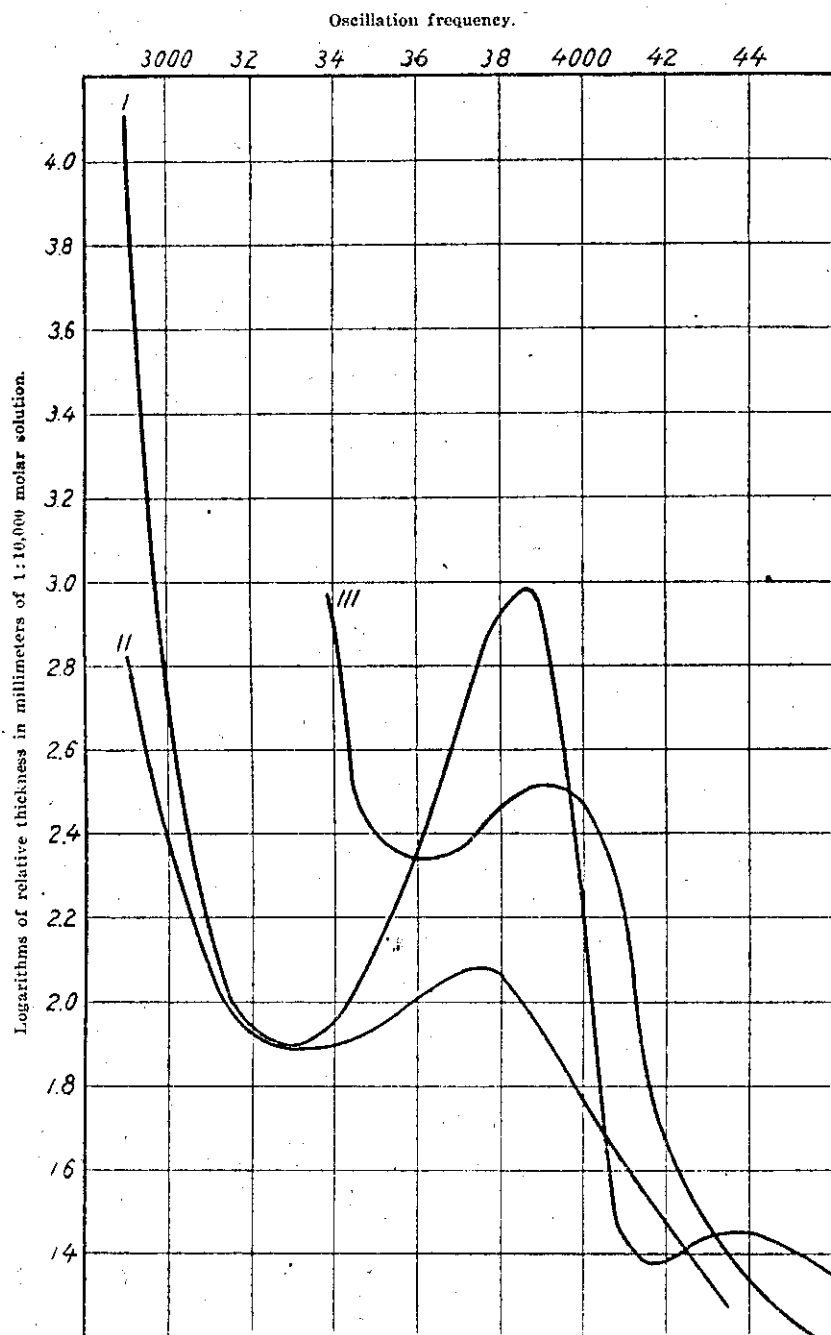
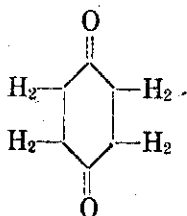


FIG. 3. Curve I. Methylsalicylate in alcohol. Curve II. Methylsalicylate in alcohol plus 500 equivalents of sodium ethylate. Curve III. Acetylmethylsalicylate in alcohol.

The color of the yellow form of ethylsuccinosuccinate is due not to an absorption band in the visible region of the spectrum, but to a band which lies so close to the visible region, heading at  $1/\lambda=2,660$ , that at the higher concentrations it broadens into the visible. Since the persistence and breadth of this band probably depend upon the relative amounts of enol and keto forms present and since the diacetyl derivative gives no band at all, it is quite possible that the pure enol form will be colorless and that the absorption band heading at  $1/\lambda=2,660$  may be absent. The equilibrium existing between the two forms in alcohol solution has so far precluded the photographing of the pure enol form without first fixing the labile hydrogen atoms. The band of the keto form is not due solely to the  $=CO$  groups in the para position but to the influence exerted upon them by the neighboring carboxyl groups. Tetrahydroquinone and its dioxime are colorless;



it seems probable, however, that these compounds will show absorption bands near the visible region of the spectrum, due in the case of the former to the mutual influence of the carbonyl groups, in a manner similar to that found in diacetyl. The neighboring carboxyl groups in ethylsuccinosuccinate may merely shift this band slightly so that it falls nearer the visible region.

Baeyer and Noyes<sup>18</sup> found that tetrahydroquinone reacts with acetyl chloride and forms a white precipitate in ether solution on the addition of sodium alcoholate and that it, therefore, may exist in two forms, the enol and keto.

Diethylsuccinosuccinate in addition to the enol and keto, may have stereoisomeric modifications, the cis and the trans forms. Since stereoisomerism is only possible when the carbon atoms to which the carboxyl groups are attached are saturated, wandering hydrogen atoms in the 1,4 positions in the keto form preclude the existence of cis and trans modifications. It seems reasonable to assume that in the keto form this change takes

<sup>18</sup> *Ber. d. deutschen chem. Ges.* (1889), 22, 2168.

place more readily when the 1, 4 hydrogen atoms are in a position to most influence the  $=\text{CO}$  groups.

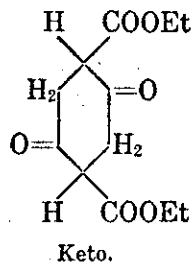
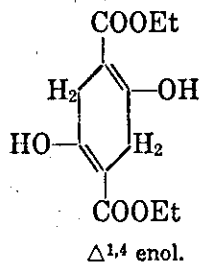
The absorption band of ethylsuccinosuccinate heading at  $1/\lambda=2,660$  is shifted to  $1/\lambda=2,400$  in the presence of sodium ethoxide. This shift in position is entirely analogous to the shift in the band of methylsalicylate and argues for a similar structure.<sup>19</sup> It has been shown that in methylsalicylate<sup>20</sup> and some related compounds the influence of the carboxyl upon the hydroxyl group is very marked and that the  $=\text{CO}$  group of the carboxyl is so affected by the neighboring hydroxyl that, in certain respects, the ester behaves more like an ether.

*Acetylmethylsalicylate.*—This compound was produced in a manner analogous to that employed by Freer<sup>21</sup> for the production of the ethyl derivative; namely, by boiling methylsalicylate with an excess of acetyl chloride. The yield seemed to be increased by the presence of a small quantity of pyridine. The ethyl ester boils at  $272^\circ$ , while we have found that the methyl derivative boils at about  $265^\circ$  with decomposition. Final purification was effected by distilling. A distillate with a constant boiling point at 7 millimeters pressure of  $122^\circ$  was obtained. This product was colorless, odorless, and produced only the faintest coloration with ferric chloride solution.

#### SUMMARY

The absorption spectra of ethylsuccinosuccinate in neutral and alkaline alcohol solutions, the diacetate in neutral solution, the diimide in neutral and acid solutions, and acetylmethylsalicylate, have been measured.

As a result of this work we believe that ethylsuccinosuccinate exists in two forms, the enol and keto, which have different melting points:



<sup>19</sup> Gibbs and Pratt, *This Journal*, Sec. A (1913), 8, 44.

<sup>20</sup> Gibbs, Williams, and Galajikian, *This Journal*, Sec. A (1913), 8, 1; and Gibbs and Pratt, loc. cit.

<sup>21</sup> *Journ. f. pr. Chemie* (1893), 47, 246.

that the pure enol form is colorless, while the keto form is yellow due to general absorption or the extension of an absorption band lying near the visible region. The fixation of the labile hydrogen atom or the saturation of the free affinities of the oxygen atoms in the para position destroys the absorption band. The behavior of this compound in the enol form is quite similar to that of methylsalicylate.



## ILLUSTRATIONS

### TEXT FIGURES

FIG. 1. *Curve I.* Diethylsuccinosuccinate in alcohol. Light yellow modification.

*Curve II.* Diethylsuccinosuccinate in alcohol. Deep yellow modification.

*Curve III.* Diethylsuccinosuccinate in alcohol plus 2 equivalents of sodium ethylate. Light yellow modification.

*Curve IV.* Diethylsuccinosuccinate in alcohol plus 2 equivalents of sodium ethylate. Deep yellow modification.

*Curve V.* Diacetyldiethylsuccinosuccinate in alcohol.

2. *Curve I.* *P*-diimide of diethylsuccinosuccinate in alcohol.

*Curve II.* *P*-diimide of diethylsuccinosuccinate in alcohol plus 2 equivalents of hydrochloric acid.

3. *Curve I.* Methylsalicylate in alcohol.

*Curve II.* Methylsalicylate in alcohol plus 500 equivalents of sodium ethylate.

*Curve III.* Acetylmethylsalicylate in alcohol.

## WATER SUPPLY FOR THE CITY OF ILOILO<sup>1</sup>

By GEORGE W. HEISE

*(From the Laboratory of General, Inorganic, and Physical Chemistry,  
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### ONE TEXT FIGURE

Iloilo, one of the largest and most important cities in the Philippine Islands, is greatly in need of a municipal water supply system, yet the problem of obtaining good water in adequate quantities is rather complex. Most of the surface waters in the vicinity are high in mineral content, and are of objectionable taste, and the artesian waters are almost all brackish, high in iron, and extremely hard. There is no suitable water available for boiler use and no supply for fire-fighting purposes. A number of the residents have accustomed themselves to drinking the water from the artesian wells, without experiencing any noticeable ill effects; many construct large rain-water cisterns; many have their drinking water carried from comparatively great distances, either from surface wells in outlying districts or from springs on Guimaras Island, across the straits from the city; many obtain distilled water from the local ice plant. As might be inferred, the situation is highly unsatisfactory. The artesian waters are so hard and brackish that they are unsatisfactory both for household and boiler use; the cistern supply, questionable at best owing to its susceptibility to contamination, is liable to fail during a long dry season; the waters carried for long distances are subject to pollution, both at the source and during transit; the distilled water is expensive and is available only for drinking purposes.

For some years the Bureau of Public Works has been developing projects for supplying the city with water. Iloilo and its environs, including Molo, La Paz, and Mandurriao, have a population of approximately 55,000 to be provided for, hence they would require, at a rough estimate based on the water consumption of Manila, a supply of about 11,350,000 liters (3,000,000 gallons) per day. Thus far three main projects have been proposed: (1) To dig enough artesian wells in the outlying districts to develop a town supply; (2) to throw a dam across Tigon River at Maasin, impounding an adequate amount of water which could be piped to the city; (3) to get water from the springs and upland water courses of Guimaras Island and to bring it to Iloilo by pipes laid beneath the straits separating the island from the mainland.

<sup>1</sup> Received for publication January 29, 1915.

I was detailed to make a "sanitary survey" of the available water supplies of Iloilo with a view toward determining the relative merits of the different projects. Accordingly a field

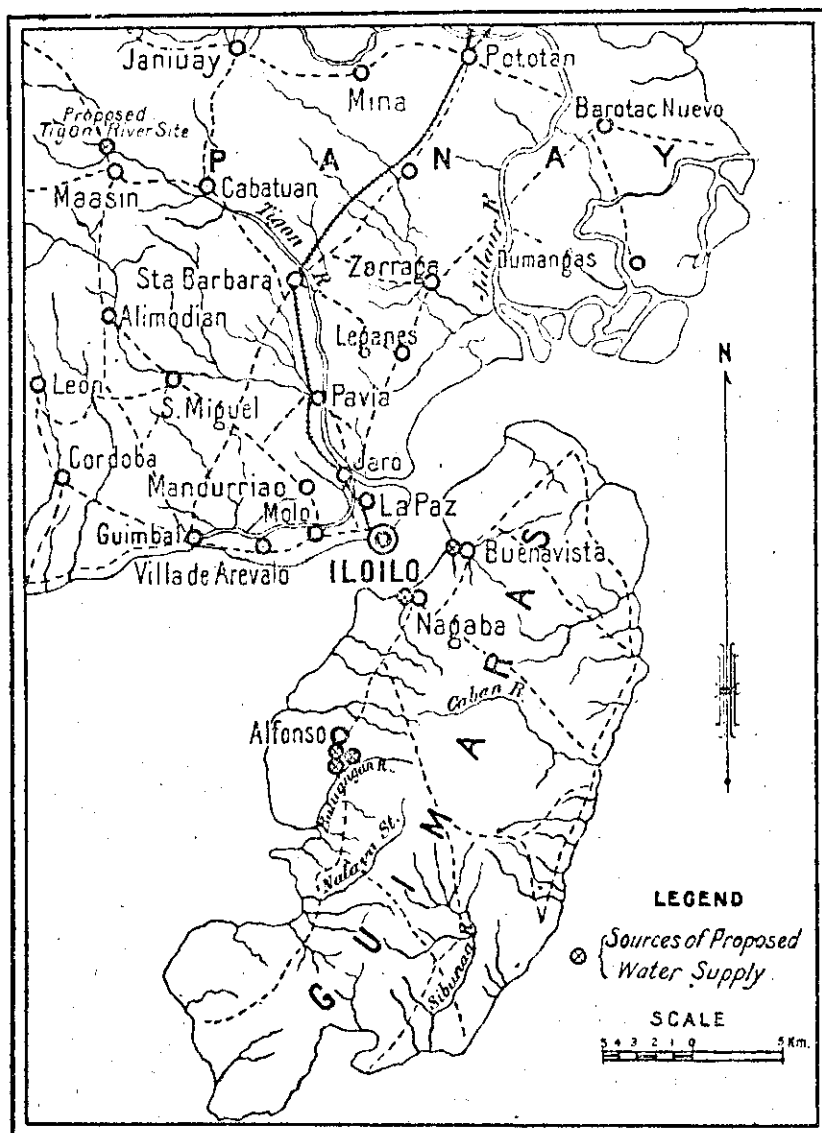


FIG. 1. Guimaras Island and a part of Panay.

investigation including chemical assays and biological examinations was undertaken in November, 1914, the results of which are detailed herewith.

The methods of chemical examination employed in this work were, with some modifications, those outlined by Leighton.<sup>2</sup> The errors and limits of accuracy involved have been discussed by the same author. In addition bacteria counts on litmus lactose agar and tests for gas-forming organisms in lactose bile agar were made with the aid of a small portable bacteriological outfit.

#### DEEP WELLS

Many wells have been drilled in the vicinity of Iloilo by the Bureau of Public Works. Most of them are from 60 to 80 meters deep, and no potable waters have been found at greater depths, although borings have been extended to over 700 meters.

The artesian well project involved drilling a battery of wells at Molo, a few kilometers from Iloilo, large enough to furnish sufficient water to supply the city. In some way it had come to be generally believed that the artesian wells already completed in that vicinity were gradually losing their salt content, and that the improvement of the water was sufficient to justify its development for a municipal supply. Just how this idea originated is not quite clear; perhaps it was due to the fact that people quickly accustom themselves to surprisingly large amounts of salt in drinking water and that their ability to detect salt by its taste is correspondingly decreased. That the salt content of the deep wells in Iloilo and its environs is not decreasing, is clearly shown by the comparative data in Table I.

TABLE I.—Chlorine content of artesian wells in Panay.

[Numbers give parts per million.]

Well No.	Chlorine content by—	
	Previous analyses (1905-1913).	Latest analyses (Nov.-Dec., 1914).
452.....	792	855
471.....	695	750
500.....	797	810
511.....	866	870
514.....	831	870
530.....	1,520	1,660
568.....	1,791	1,800
428.....	725	790
Customhouse well No. 3.....	867	925
490.....	275	318
480.....	356	376
580.....	390	600

<sup>2</sup> Water Suppl. & Irrig. Papers, U. S. Geol. Surv. (1905), No. 151.

Although no great accuracy is claimed for the most recent analyses, since part of them were made by field methods, the results may be considered conclusive, especially as a number of determinations were checked volumetrically and showed good agreement. The detailed analyses of the artesian well waters of Iloilo and vicinity, as performed during the course of the present investigation, are given in Table II.

Color is rated in approximate accordance with the Hazen platinum-cobalt color standard.<sup>3</sup>

As will be seen from the analyses, the waters listed are all brackish.<sup>4</sup> Some of the artesian wells show an appreciable variation in their flow, being influenced by the tides; in fact, some are intermittent and flow only at high tide. The quality, too, of these waters, shows certain variations, but whether the changes noticed are also dependent on the tides has not yet been established. It is clear that seepage from the ocean<sup>5</sup> is not a factor. The absence of sulphates is a marked peculiarity. Barber<sup>5</sup> has already pointed out that flowing artesian wells are practically sterile, and this series of tests confirms his conclusions. None of the drilled wells examined showed an excessive bacteria count.

In view of their high mineral content, their brackishness, their mildly laxative properties, and their excessive hardness, it does not seem advisable to try to develop any of these waters as a source of municipal supply.

#### MAASIN

The Maasin proposition involves the installation of the type of system which has already been found successful at Manila and Cebu; namely, the impounding of the water from a river and the reservation of the watershed drained by that river from settlement and trespass.

The advantages of the Maasin project are the certainty of an adequate supply of water throughout the year and the possibility of supplying other towns, between Maasin and Iloilo, with much-needed water systems; its disadvantages are the distance (at least 25 kilometers) which the water must be piped, and the cost of the enterprise (more than 2,000,000 pesos).

<sup>3</sup> *Am. Chem. Journ.* (1892), 14, 300.

<sup>4</sup> All the waters in Table II, with the possible exception of Nos. 7, 8, 13, and 15, and perhaps one or two others, were being used for drinking purposes. They are certainly more wholesome than any other natural waters available in the districts they supply.

<sup>5</sup> *This Journal*, Sec. B (1913), 8, 443.

TABLE II.—Deep wells, Iloilo and vicinity.

[Numbers give parts per million.]

Tracing No.	Laboratory No.	Location.	Artesian well No.	Depth.	Flows or pumps (liters per minute).	Color.	Turbidity as SiO <sub>2</sub> .	Chlorides (Cl).	Carbonates as Na <sub>2</sub> CO <sub>3</sub> .	Bicarbonates as CaCO <sub>3</sub> .	Sulphates as SO <sub>2</sub> .	Alkalinity as CaCO <sub>3</sub> .	Iron (Fe).	Calcium (Ca).	Total hardness as CaCO <sub>3</sub> .	Bacterial count, per cc.	Acid formers.	Gas formers.
				m.														
1	7	Provincial building, Iloilo .....	452	75	Flow slight or nil.....	(*)	---	855	0	28.6	0	28.6	6.0	80±	232	10	0	0
2	13	Calles Mabini and Gral. Luna, Iloilo .....	471	77	Pumps .....	1.5	0	750	0	43.0	0	43	4.0	---	206	---	---	---
3	9	Public market, Iloilo .....	500	76	do .....	(*)	0	810	0	50.0	0	50	10.0	---	388	---	---	---
4	8	Plaza Libertad, Iloilo .....	511	62	Flows only at high tide.	---	0	870	0	72.5	0	72.5	4.0	---	370	---	---	---
5	3	Calle Ortiz, Iloilo.....	514	63	Flows 70.....	---	---	870	0	64.5	0	64.5	8.0	100±	296	0	0	0
6	10	Landon mess, Calle Remedios, Iloilo.....	523	87	Pumps .....	0.8	0	1,060	0	35.0	0	35.0	2.0	---	442	---	---	---
7	20	Off Calle Rosario (M. Zerrudo) .....	530	73	do .....	0.7	0	1,660	0	32	0	32.3	4.5	---	192	---	---	---
8	17	Plaza Goiti and Ledesma, Iloilo .....	568	72	do .....	0	0	1,800±	0	44.0	(*)	44.0	10.0	---	720	---	---	---
9	11	Calles Lanao and Yznart, Iloilo .....	592	79	Flows 15.....	1.0	0	930	0	51.0	0	51.0	2.0	---	240	6	0	0
10	15	Calles Ledesma and Rizal, Iloilo.....	600	79	Flow slight.....	0.7	0	600	0	31.0	0	31.0	6.5	---	260	<40	0	0
11	12	Assumption College, Iloilo .....	428	77	Flows 19.....	1.5	0	790	0	31.0	0	31.0	4.0	---	234	0	0	0
12	19	Customhouse, Iloilo .....	---	---	Flows 10.....	0	0	925	0	50.0	0	50.0	4.0	---	320	---	---	---
13	25	Iloilo Electric Co., Iloilo.....	---	78	Flows only at high tide.	1.0	0	1,280	0	50.0	0	50.0	12.0	---	328	---	---	---
14	14	On proposed street near Calle Ledesma, Iloilo.	---	76	Flows 55.....	0.5	0	960	0	43.0	0	42.8	6.0	---	280	10	0	0
15	21	Calle Rosario, No. 26, Iloilo (J. Javellano) .....	---	120	Pumps .....	0.5	0	1,550	0	46.0	0	46.1	7.5	---	166	---	---	---
16	5	Calles R. Mapa and Cementerio, Mandurriao .....	490	86	Pumps 110.....	3.5	0	318	34.8	12.5	0	37.5	2.5	20±	58.0	100±	20	0
17	1	Calles Nueva and Antigua, Molo .....	480	60	Flows 3.5±.....	---	0	376	0	89.5	0	89.5	2.2	---	230	10	0	0
18	2	Calle Antigua, near bay, Molo.....	580	54	Flows 35.....	---	---	600	0	72.5	0	72.5	1.0	---	400	10	0	0

\* Trace.

From a chemical point of view, the water is potable, and since it comes from a sparsely settled watershed, which could be closed to settlement and guarded against trespass, it can doubtless be kept uncontaminated. The chemical analysis of the Tigon River water is as follows:

TABLE III.—*Chemical analysis of the Tigon River water.*

Physical characteristics	Normal.
Turbidity	Nil.
Color	Nil.
Total solids	390
Fixed	290
Volatile	100
Organic matter	Trace.
Alkalinity as $\text{CaCO}_3$	50
Iron (Fe)	0.7
Magnesium (Mg)	Little.
Normal carbonates as $\text{Na}_2\text{CO}_3$	Nil.
Bicarbonates as $\text{CaCO}_3$	50
Sulphates as $\text{SO}_4$	54
Chlorides (Cl)	16
Total hardness as $\text{CaCO}_3$	140
Estimated encrustants	140

#### GUIMARAS ISLAND

Guimaras Island is well supplied with water. In the coralline limestone formations near the coast there are many springs which have excellent local reputations; farther inland and upland there are streams which have an apparent abundance of clear soft water. During the Spanish régime, the waters from various springs were brought into great stone baths, some of which still exist.

The single attempt to drill an artesian well on Guimaras proved a failure. Although a depth of over 200 meters was attained, no potable water was encountered in any appreciable quantities.

Table IV shows the analyses of typical water supplies.

The "probable encrustants" were determined in accordance with the formula given by Dole.\* The "classification for boiler use" is more or less arbitrary.

Chemically these waters appear to be suitable for the Iloilo supply. Guimaras Island is so sparsely populated that it should be very easy to prevent the contamination of any of the sources listed.

\* *Water Suppl. & Irrig. Papers, U. S. Geol. Surv. (1910), No. 254, 232.*

TABLE IV.—*Waters of Guimaras Island.*

[Numbers give parts per million.]

Tracing No.	Laboratory "I" No.	Location.	Source.	Color.	Turbidity as SiO <sub>2</sub> .	Chlorides (Cl).	Carbonates as Na <sub>2</sub> CO <sub>3</sub> .	Bicarbonates as CaCO <sub>3</sub> .	Sulphates as SO <sub>4</sub> .	Alkalinity as CaCO <sub>3</sub> .	Iron (Fe).	Total hardness as CaCO <sub>3</sub> .	Probable encrustants.	Classification for boiler use.	Remarks.
1	26	Dallran, Buenavista	Spring	0	0	10.5	0	48.5	(a)	48.5	1.0	246	145	Fair	Less than 60 bacteria per cc.; no acid or gas formers.
2	27	Buenavista	Taingban Cave	0	0	9.0	0	46.2	(a)	46.2	4.0	300	171	do	
3	28	Near river at Buenavista	Spring	0	0	24.0	0	50.0	(a)	50.0	1.0	288	165	do	
4	29	Large cement bath, Nagaba	do	0	0	11.5	0	49.1	(a)	49.1	5.0	336	190	Fair to poor	
5	30	Old broken-down bath, Nagaba	do	0	0	13.0	0	50.0	(a)	50.0	5.0	335	188	do	
6	31	Eight kilometers from Nagaba southeast of hacienda.	Waterfall, river	0	0	8.0	0	25.0	(a)	25.0	1.0	40	32	Excellent	Fifty organisms per cc.; no acid or gas formers.
7	32	Near hacienda	Spring	0	0	8.5	0	50.0	(a)	50.0	0.66	276	160	Fair	
8	33	South of hacienda	River	0	0	6.5	0	17.0	(a)	17.0	0.85	46	31	Excellent	

\* Trace.



At the present time weirs have been established to determine how much water is available from the various water sources at different seasons of the year. It is quite possible that enough water may be developed from the upland sources to enable the installation of a direct gravity system for Iloilo.

The Guimaras project is an attractive one, because, if feasible, it means a supply of water for Iloilo at comparatively low expense. The distance across the straits is something over 3 kilometers, but in spite of the added difficulty and expense involved in piping the water under the sea, the estimated cost of the Guimaras project is only about one-tenth that of the Maasin enterprise.

#### CONCLUSIONS

The chemical character of the artesian waters is such that their development as a source of municipal water supply does not seem advisable.

The Maasin and the Guimaras Island projects are both feasible, so far as the quality of the water is concerned.

## ILLUSTRATION

### TEXT FIGURE

FIG. 1. Map of Guimaras Island and a part of Panay Island, P. I.

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## BOILER WATERS OF ILOILO PROVINCE<sup>1</sup>

By GEORGE W. HEISE

*(From the Laboratory of General, Inorganic, and Physical Chemistry,  
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A good illustration of the practical value of, and the necessity for, a systematic study of Philippine water supplies was furnished during the course of a recent field investigation of the waters available for the municipal supply of Iloilo, on Panay Island.

Iloilo, now numbering over 50,000 inhabitants, is one of the largest and most important cities in the Philippine Islands; yet it has no water supply system. Its needs are supplied for the most part by a number of brackish artesian wells, by surface wells, and by rain-water cisterns. The users of boiler water seem never to have been able to obtain waters suitable for their needs. Practically without exception, the waters extensively used at the present time are uniformly bad, and there have been developed no sources of good water within a reasonable radius of the city of Iloilo. The artesian wells of Iloilo and vicinity are almost out of the question for boiler use, owing to the excessive amounts of salt and scale-forming ingredients which they contain, and the surface supplies are almost as bad. A representative of one of the larger firms in Iloilo asserted that his company was spending 500 pesos a month for boiler parts and wear and tear on equipment, due to the use of bad boiler water. There was no apparent reason to believe that the figure mentioned was exaggerated, indicating that the waste due to the use of improper water for industrial purposes amounted to several thousand pesos per month for the city of Iloilo alone. Most of the boiler water used is taken from Salog River at Jaro, whence it is piped to Iloilo. Although known to be of very poor quality, it was the best water available, and was accordingly much used.

No systematic study of the available water supplies had ever been attempted. A preliminary investigation indicated that there must be sources of good water available for use in Iloilo Province either unknown or undeveloped. In the regular course

<sup>1</sup> Received for publication, January 26, 1915.

TABLE I.—Analyses of waters of Iloilo Province.

[Numbers represent parts per million.]

Tracing No.	Laboratory No.	Location.	Source of supply.	Color.	Turbidity as SiO <sub>2</sub> .	Alkalinity as CaCO <sub>3</sub> .	Total solids.	Fixed solids.
1	31	Guimaras	Waterfall, 8 kilometers southeast of Nagaba.	0	0	25.0		
2	49	Dao, Capiz	Sump	100	(*)	33.4	200	100
3	62	Bridge 27-8, Philippine Rwy. Co	Slough	50	(*)	72.6	100	105
4	50	Buntog, Capiz	Panay River	100	29	34.4	125	85
5	64	At telegraph pole 15-10, Philippine Rwy. Co	Slough	50	25	51.7	120	30
6	53	Railroad bridge 56-9, Lamunang, Iloilo	Lamunang River			33.4	212	128
7	58	Crossing Passi-Calinog provincial road, Iloilo	do	0	0	50.0	260	140
8	48	Mambusao, railroad bridge 90-5	Mambusao River	25	0	50.0	280	160
9	59	Passi, Iloilo (above juncture with Lamunang River)	Jalaur River	0	(*)	30.8	130	110
10	55	Passi, Iloilo, railroad bridge 53-6	do		400	31.8	514	328
11	39	Golf Club, Santa Barbara, Iloilo	Spring	0	0	66.7		
12	60	Philippine Rwy. Co. bridge 46-6	Ulian River		(*)	46.2	260	170
13	34	Beyond Pototan, crossing of provincial road with river.	Jalaur River	0	0	54.5		
14	51	North of Dumarao, Capiz	Stream	25	0	47.5	310	215
15	52	Dumarao, Capiz	Sump	25	(*)	50.0	305	225
16	36	At river-crossing of provincial road between Santa Barbara and Janinay.	Tigon River	0	0	50.0	330	290
17	61	Bridge 29-5, Philippine Rwy. Co	Abangay River	50	(*)	54.5	535	405
18	63	Bridge 17-4, Philippine Rwy. Co	Tigon River	0	(*)	51.7	435	315
19	45	Pototan, Iloilo	River	0	0	54.6	405	370
20	65	Pavia, Iloilo	Tigon River	0	0	41.6	365	285
21	46	Capiz, Capiz	Sump			46.8	660	420
22	56	Pavia bridge, Iloilo	River	0	0	36.4	440	360
23	23	Trade School, Iloilo	Surface well	0	0	50.0		

24	54	Passi, Iloilo	Sump	10	0	32.2	700	485			
25	44	Calle Jaena, next to municipio of Pototan, Iloilo	Surface well	0	0	46.0					
26	16	Jaro, Iloilo	Salog River	0	0	32.0					
27	4	Near monument at Plaza Libertad, Iloilo	Surface well		0	54.5					
28	22	At army post, within 50 meters of the bay, Iloilo, Iloilo	do	0	113	44.5					
29	37	At plaza, Santa Barbara, Iloilo	Artesian well	125	0	75.0	1,180	1,040			
30	5	Calles R. Mapa and Cementerio, Mandurriao, Iloilo	Artesian well 490	175	0	37.5					
31	3	Calle Ortiz, Iloilo	Artesian well 514			61.5	2,260	2,005			
32	25	Iloilo Electric Co., Iloilo	Artesian well	50	0	50.0					
33	10	Calle Remedios, Iloilo	Artesian well 523	40	0	35.0					
34	17	Plaza Goiti and Ledesma, Iloilo, Iloilo	Artesian well 563	0	0	44.0					

Tracing No.	Volatile on ignition.	Calcium (Ca).	Iron (Fe).	Sulphates as SO <sub>3</sub> .	Chlorides (Cl).	Normal carbonates as Na <sub>2</sub> CO <sub>3</sub> .	Bicarbonates as CaCO <sub>3</sub> .	Total hardness as CaCO <sub>3</sub> .	Probable encrustants.	Classification for boiler use.	Remarks.
1		0	1.00	(*)	8.0	0	25.0	40	35	Excellent	Contains much organic matter.
2	100	39	2.70	0	8.0	0	33.4	66	50	Good	
3	85	(*)	2.00	(*)	11.0	0	72.6	68	75	do	
4	40	40	0.80	18.0	5.0	0	34.4	80	75	do	Do.
5	90	(*)	4.00	0	19.0	0	51.7	52	55	do	
6	84	(?) 96	0.35	10.5	5.0	0	33.4	94	75	do	
7	120	81	0.50	10.0	7.5	0	50.0	100	85	do	Clears rapidly by sedimentation.
8	120	70	2.00	14.5	5.5	0	50.0	100	90	Fair	
9	80	(?) 96	0.35	19.0	8.0	16.9	15.4	128	90	do	
10	186	83	2.70	15.5	6.5	0	31.8	100	80	do	
11		(?) 100	0	(*)	8.0	0	66.7	131	100	do	
12	90		0.35	19.0	10.0	0	46.2	112	95	do	
13			0.50	29.0	10.0	0	54.5	120	115	do	
14	85		0.25	25.0	6.5	0	47.5	168	130	do	

\* Trace.

TABLE I.—Analyses of waters of Iloilo Province—Continued.

Tracing No.	Volatile on ignition.	Calcium (Ca).	Iron (Fe).	Sulphates as SO <sub>3</sub> .	Chlorides (Cl).	Normal carbonates as Na <sub>2</sub> CO <sub>3</sub> .	Bicarbonates as CaCO <sub>3</sub> .	Total hardness as CaCO <sub>3</sub> .	Probable encrustants.	Classification for boiler use.	Remarks.
15	80	-----	1.50	27.5	11.5	0	50.0	152	125	Fair -----	Contains some organic matter.
16	100	-----	0.65	54.0	16.0	0	50.0	140	145	do -----	
17	130	-----	1.00	19.0	102.5	0	54.5	100	95	do -----	
18	120	110	0.50	22.5	14.0	0	51.7	250	170	Fair to poor -----	
19	35	(?) 110	6.00	50.0	14.0	21.2	25.5	138	125	Fair -----	
20	80	-----	2.00	79.0	17.0	19.3	25.0	146	165	do -----	
21	240	-----	0.35	125.0	85.0	0	46.8	106	185	Poor -----	
22	80	-----	(*)	100.0	16.0	0	36.4	192	200	do -----	
23	-----	-----	0	11.0	70.5	0	50.0	212	140	Fair -----	
24	215	-----	0.35	68.5	117.0	0	32.2	192	170	Poor -----	
25	-----	-----	1.70	73.0	85.0	0	46.0	282	230	do -----	
26	-----	-----	0.30	144.0	154.0	0	32.0	336	340	Bad -----	
27	-----	-----	1.00	350.0	790.0	0	54.5	440	545	Very bad -----	
28	-----	-----	24.00	>600	8,150.0	26.5	19.4	820	1,020	do -----	
29	140	0	12.00	0	242.0	60.5	17.5	17	17	(?) -----	Too high in nonencrusting solids for good boiler water. Do.
30	-----	<20	2.50	0	318.0	34.8	12.5	58	35	(?) -----	
31	255	119	8.00	0	870.0	0	64.5	296	185	Bad -----	
32	-----	-----	12.00	0	1,280.0	0	50.0	828	190	do -----	
33	-----	-----	2.00	0	1,060.0	0	35.0	442	240	Very bad -----	
34	-----	-----	10.00	(*)	1,835.0	0	44.0	720	390	do -----	Becomes turbid on standing.

\* Trace.

of the work a number of water supplies were found which might be used to advantage, and in order to make the results of this work available the most significant data are tabulated herewith.

Most of this work was done in the field, for the most part in accordance with the methods outlined by Leighton,<sup>2</sup> by whom the sources of error and the accuracy of these methods have been discussed. "Color" is rated in terms of the Hazen<sup>3</sup> platinum-cobalt standard. The "probable encrustants" were calculated in accordance with the formula given by Dole.<sup>4</sup> The "classification for boiler use" is more or less arbitrary.

Although these data are only approximate, they give a fairly good idea of the industrial water supply situation in Iloilo, and indicate that there are a number of sources which will yield good boiler water.

Some of these waters should be quite suitable for boiler purposes without any treatment; most of them could be made into excellent boiler waters by preheating or by inexpensive chemical treatment. It will be noted that the "Jaro" water is one of the worst on the list. The sources listed for the most part are surface supplies; hence, it is possible that change of season might introduce or cause variations in chemical quality. All of the analyses were made in November and December, 1914; that is, after the dry season was well along; hence, another series of analyses should be made, preferably during the rainy season, to determine whether any changes occur great enough to affect the fitness of these waters for boiler purposes.

<sup>2</sup> *Water Suppl. & Irrig. Papers, U. S. Geol. Surv.* (1905), No. 151.

<sup>3</sup> *Am. Chem. Journ.* (1892), 12, 300.

<sup>4</sup> *Water Suppl. & Irrig. Papers, U. S. Geol. Surv.* (1910), No. 254, 232.

## A PRELIMINARY CHECK LIST OF PHILIPPINE MINERALS<sup>1</sup>

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The following 113 mineral species and varieties comprise all those known with certainty to us to occur in the Philippines. There are others whose presence we suspect, but which have not been definitely identified. For instance, tin, native brass, and diamonds are said to exist here, but this laboratory has no authoritative knowledge of them.

All the minerals herein mentioned are in the collections of the Bureau of Science, and have been collected for the most part during the American régime. The collections of the old Spanish Mining Bureau were almost worthless when they passed into the hands of the Americans. Whether the best specimens had been transferred elsewhere at the outbreak of hostilities we do not know, but we have reason to suspect such to have been the case.

Three other mineral collections in the city of Manila have been consulted; namely, that of the Ateneo de Manila of the Jesuit Order, that of the Santo Tomás University of the Dominican Order, and lastly that of the Ateneo de Rizal, but we have found only a very few specimens which were not in our own collection. As there is some doubt also about the localities of some of the minerals in those collections, we have purposely omitted several species.

Our acknowledgement of assistance from the curators of these institutes is hereby gratefully made.

It will be noted that many of the minerals in the following list have no economic value, but the fact that a substance has no present commercial value is no reason for excluding it from a catalogue. The future will undoubtedly see a number of minerals now thought to be of little or of no use to man become of great commercial value. For instance, when the large deposits of concentrated iron oxides, like hematite and limonite, become exhausted we shall be forced in all probability to turn to the iron-bearing silicates of too low a grade to be worked economically at the present time. The mineral leucite with its 21 per cent of potash is a valuable prospective source of this important

<sup>1</sup> Reprinted from *Min. Resources P. I. for the year 1913, Bur. Sci.* (1914).



ingredient of the soil, but only until recently has any one thought seriously of extracting it.

We have before us the list of minerals of Taiwan (Formosa) by Okamoto, of the educational bureau of that island. In this list he gives 50 minerals, less than half the number we have in the following list. Six of these we have not yet found in the Philippines, while there are 3 others which we suspected to be here but have not certainly determined.

We take this opportunity to urge all the mining men and students of the various schools and colleges to send specimens of any minerals which they may think new or interesting to the Bureau of Science. It is reasonable to expect that when more persons shall become interested in this line and more observant of natural objects this list will be greatly augmented. We are already greatly indebted to many of our friends of the mining community for valuable specimens.

It is to be regretted that up to the present we have not made many studies of a mineralogic nature, as more pressing investigations in the mining fields have prevented us from doing so. The compilation of this preliminary list has suggested several subjects which can be profitably taken up in the future.

#### CHECK LIST OF PHILIPPINE MINERALS

**Actinolite**— $\text{Ca}(\text{Mg}, \text{Fe})_3\text{Si}_4\text{O}_{12}$ .

This mineral occurs as acicular green crystals in the crystalline schists of Ilocos Norte. It is classed as one variety of asbestos in the trade. There is no production in the Philippines.

**Agate**— $\text{SiO}_2$ .

Agate is found in many parts of the Archipelago where silicification has occurred. Occasionally some specimens suitable for polishing are found. There is no production in the Philippines.

**Albite.** (See Plagioclase).

**Altaite**— $\text{PbTe}$ .

This mineral occurs intimately mixed with sylvanite and free gold in specimens from the Tumbaga mine, Ambos Camarines. It is tin white, sometimes with a bronze tarnish, and occurs as negative crystals or pseudomorphs after quartz crystals or fragments. Development work exists only at this mine.

**Amethyst**— $\text{SiO}_2$ .

Some large crystals have been found in Palawan, but this mineral is not common in the Philippine Islands. One large specimen of amethyst crystals from Mount Tumarbon, Palawan,

can be seen in the Santo Tomás Museum. When perfect it is used as a gem. There is no production in the Philippine Islands.

**Analcite**— $\text{NaAl}(\text{SiO}_3)_2 + \text{H}_2\text{O}$ .

This mineral occurs as an alteration product of leucite in some volcanic rocks of limited distribution in Masbate.

**Andesine.** (See Plagioclase).

**Anorthite.** (See Plagioclase).

**Anthophyllite**— $(\text{Mg}, \text{Fe})\text{SiO}_3$ .

This mineral is a variety of amphibole in long dirty white to brownish fibers, and is associated with serpentine and asbestos. It occurs in Ilocos Norte. In some cases it could be used as a substitute for asbestos. There is no production in the Philippines.

**Apatite**— $\text{Ca}_5(\text{Cl}, \text{F})(\text{PO}_4)_3$ .

Apatite occurs as large yellowish crystals in small amounts in metamorphic rocks near Pasuquin, Ilocos Norte, and also in minute crystals in many igneous rocks in the Philippine Islands. It is valuable for fertilizer if found in large enough quantities. There is no production in the Philippines.

**Aragonite**— $\text{CaCO}_3$ .

The mineral is found so far in one locality, Talim Island, Laguna, in long clear crystals in vugs in basalt. It has no economic value.

**Arsenic**—As (metallic).

This mineral is deposited presumably from hot springs in the form of kidneys (reniform). It is found near Buguias, Mountain Province. There is no local use for arsenic.

**Asbestos**— $\text{H}_2(\text{Mg}, \text{Fe})_3\text{Si}_2\text{O}_{10}$ . (?)

Asbestos is associated with serpentine in Ilocos Norte. No first-grade asbestos has yet been found. It consists practically of longitudinal fibers. One small sample of cross fiber (see Chrysotile) is in our collection. There is no production in the Philippines.

**Asphaltum**—Complex series of hydrocarbons.

One small specimen was brought in from the Eastern Cordillera, Luzon, which is of doubtful authenticity.

**Augite**— $(\text{Mg}, \text{Fe})(\text{Al}, \text{Fe})_2\text{SiO}_6$ .

This mineral is one of the pyroxene group of silicates—common as a rock mineral. Augite has no economic value at present.

**Azurite— $\text{Cu}_2(\text{OH})_2(\text{CO}_3)_2$ .**

Azurite occurs as minute blue crystals in some copper deposits of Pangasinan, Batangas, and Mindanao.

**Baltimorite— $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$ .**

Baltimorite is a white to bluish fibrous mineral associated with serpentine. It is found in Ilocos Norte. It could be used for steam packing and roofing material. There is no production in the Philippines.

**Barite— $\text{BaSO}_4$ .**

Barite is reported from Mancayan as a vein mineral by A. J. Eveland.

**Basonite— $\text{SiO}_2$ .**

This mineral is a velvet-black variety of flint known as "touch stone" or lydian stone. It could be used for testing the purity of gold. One sample, No. 176, is in the collection of the Ateneo de Manila.

**Beryl (emerald)— $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ .**

Small and imperfect specimens are reported from Mindanao, but nothing definite is known regarding the locality.

**Biotite— $(\text{H}, \text{K})_2(\text{Mg}, \text{Fe})_2\text{Al}_2\text{Si}_3\text{O}_{12}$ .**

Biotite occurs in various igneous rocks in the Philippines in small crystals, principally in Paracale granite. No economic deposits are known here.

**Bituminous coal—Complex composition, principally oxygenated hydrocarbons.**

Bituminous coal is found in seams from a few centimeters to several meters thick in Cebu and Mindanao. Formerly there was a moderate production in Cebu. There is none in Mindanao. One specimen from Dumanquilas Bay, Mindanao, shows columnar structure.

**Bornite— $\text{Cu}_5\text{FeS}_4$ .**

Bornite occurs massive to finely crystalline in quartz veins. It is probably secondary in origin. This mineral is found in several of the copper deposits in the Islands. An excellent sample comes from Quien Sabe claim, Suyoc, Mountain Province. There is development work in the Philippines but no production.

**Calcite— $\text{CaCO}_3$ .**

Calcite is generally massive without crystalline faces, but some splendidly crystallized samples of "dog tooth" spar have

been found. It is frequently associated with primary and secondary manganese minerals, and is also frequently associated with quartz in ore veins, there being a progression from quartz to quartz-calcite, probably the result of lowering of temperature and pressure. Calcite occurs also as a secondary mineral in igneous rocks; also, as stalactites, stalagmites, and travertine. Marble is found in Romblon and crystallized limestone at Montalban. The mineral is used to manufacture quicklime for sugar refining. Marble is used for monuments and building purposes.

Chalcedony— $\text{SiO}_2 + \text{H}_2\text{O}$ .

Chalcedony occurs in irregular milky-white patches in jaspers and other rocks in various parts of the Islands.

Chalcocite— $\text{Cu}_2\text{S}$ .

Chalcocite is a massive gray mineral usually secondary in the upper zones. It is found in Misamis, Mindanao, and Mountain Province, Luzon. There is no production in the Philippines.

Chalcopyrite— $\text{CuFeS}_2$ .

Chalcopyrite is the most universally distributed ore of copper. It is found as small crystals in a large number of quartz veins, and is associated mainly with galena and usually crystallizes after galena. It is found in small quantities in all of the mining districts. No commercial deposits are known in the Philippines.

Chert— $\text{SiO}_2$ .

Chert occurs as nodules in various formations in many parts of the Archipelago, also as radiolarian cherts, probably of Jurassic age. It is well developed in Palawan, Panay, Ilocos Norte, and Balabac, and is probably equivalent to the radiolarian "hornfels" of central Borneo. It has no economic use.

Chlorite— $\text{H}_3\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{18}$ .

Chlorite occurs as fine, green fibrous masses as an alteration product in many igneous rocks. It has no economic use.

Chromite— $\text{FeOCr}_2\text{O}_3$ .

Chromite occurs associated with serpentine in heavy granular masses with mottled black and green appearance in Antique Province, Panay. There is some prospecting but no production.

Chrysoprase— $\text{SiO}_2$  (colored by nickel oxide).

Chrysoprase occurs as beautiful leek-green pebbles in a river near Butuan, Mindanao. One specimen, No. 180, is in the collection of the Ateneo de Manila. This mineral could be used as a gem.

**Chrysotile**— $H_3(Mg, Fe)_3Si_2O_6$ .

Chrysotile occurs as white to greenish silky fibers. Some inferior specimens have been found in Ilocos Norte. Short cross fibers of from 2 to 3 centimeters in length have been found. There is no production, but indications are promising.

**Cinnabar**— $HgS$ .

Minute red crystals of cinnabar were found in a few samples from Batwaan Creek, Benguet, Luzon. Cinnabar remains in the pan with the gold. It is reported from Mount Isarog, Ambos Camarines. This mineral forms under surface conditions, and is connected with volcanic activity. It is not mined in the Philippines.

**Copper**— $Cu$  (metallic).

Native copper occurs as irregular, partly crystalline masses and as round shot in alluvium; there are 3 type occurrences: (1) Amygdoloids in extrusives, in Masbate; (2) in alluvials of Malaguit River, Ambos Camarines; (3) reported in some quartz veins in Masbate. Native copper was probably used formerly by Igorots to make pots. It is not used at present.

**Corundum**— $Al_2O_3$ .

Corundum occurs as pebbles in placers in Nueva Ecija, Luzon.

**Crocoite**— $PbCrO_4$ .

Crocoite occurs in characteristic small orange-red monoclinic crystals in Labo, Paracale district, Ambos Camarines, Luzon. It is associated with galena-bearing rocks, and is not abundant.

**Cuprite**— $Cu_2O$ .

Cuprite occurs as small clear red crystals in the surface ore of a copper deposit in Antique Province, Panay.

**Diallage**—A nonaluminous pyroxene.

Diallage is a common constituent of gabbros in the Philippines. It has no economic value.

**Enargite**— $Cu_3AsS_4$ .

Enargite is probably secondary in copper deposits. It occurs massive and in small gray crystals with luzonite in the old Santa Barbara mine at Mancayan, Lepanto, Luzon. It is mined and smelted by Igorots. Formerly there was a considerable production by a Spanish company; at present it is not important.

**Epidote**— $HCa_2(Al, Fe)_3Si_3O_{12}$ .

Epidote is very rare. It occurs as yellowish grains or in more

or less amorphous masses in a few igneous rocks. It has no economic value.

**Galena—PbS.**

Galena is found in veins only. It is lacking in the walls. Galena is formed generally later than pyrite. As a rule, it is crystallized. It is associated with zinc and pyrite in quartz veins, rarely in calcite veins. It frequently carries silver, but rarely gold. It is nearly always primary. Galena is resistant to decomposition. This mineral is found in veins in Suyoc, Mountain Province; in Batangas; Cebu; Marinduque; Paracale; and Surigao. During the Spanish régime galena was mined to a limited extent in Cebu, but is not mined at the present time.

**Garnet—Complex silicates with Fe, Mg, Mn, and Ca as interchangeable bases.**

The common species, andratite, occurs rarely in the Philippines as minute wine-red granules in a rock from Bulacan, Luzon. It has no economic value.

**Gilsonite—Complex hydrocarbon.**

Gilsonite is found in the northern part of Leyte Province adjacent to petroleum seeps in Miocene shale and sandstone. There is no production in the Philippines, but the Leyte deposit is being explored.

**Gold—Au (metallic).**

Gold occurs associated with pyrite and rarely with galena. It usually occurs as metallic gold in quartz and in calcite veins as wires, plates, grains, and crystals; abundantly distributed in placer as perfect crystals, wires, and rounded grains; and is occasionally found as nuggets weighing from 10 to 30 grams. Traces of gold are found in most rocks carrying pyrite. Gold is found in paying quantity in veins in Suyoc and Baguio, Mountain Province; Paracale and Mambulao, Ambos Camarines; and Aroroy, Masbate. It is found in paying quantity in placer in Suyoc, Mountain Province; Peñaranda district, Nueva Ecija; Umaeri, Tayabas; Paracale, Mambulao, and Malaguit, Ambos Camarines; Cansuran, Surigao; Hibong River, and other localities along the Agusan River, Mindanao in Misamis Province; and in Mindoro.

**Graphite—C.**

Graphite is reported as occurring in "graphite clay" in Bulacan.

Guano— $P_2O_5$  with impurities.

Guano occurs as a coarse brownish earth in limestone caves in many parts of the Archipelago, principally along sea coasts. A small amount is collected, which is sold to Japanese exporters.

Gypsum— $CaSO_4$ .

Gypsum occurs generally in small tubular crystals as incrustations on volcanic rocks near solfataras; also, in finely granular form in the Loboo Mountains, Batangas, Luzon. There is no production, and the quantity is apparently limited.

Hematite— $Fe_2O_3$ .

Hematite is found in irregular "pockets" with magnetite, pyrite, chalcopryrite, and quartz in crystalline rocks of the Eastern Cordillera of Luzon; also, in veins cutting limestone. It occurs from Mambulao Bay, Ambos Camarines, to northern Bulacan, Luzon. The grade of this ore is excellent. It is smelted by Filipinos in crude blast furnaces to make plowshares.

Hornblende— $RSiO_3$ , R being more than one of the elements Ca, Mg, Fe, Al, Na, and K.

Hornblende is abundant in many igneous rocks as black crystals varying in size from microscopic to 2 or 3 centimeters in length. It is of no economic value.

Hypersthene— $(FeMg)SiO_3$ .

Hypersthene occurs in certain varieties of andesite in many localities. It is distinguished by its pleochroism (colorless to delicate pink) under the microscope. Hypersthene has no economic value.

Iddingsite—Exact composition not known.

Iddingsite occurs as alteration of olivine in rocks from three localities, Mount Mariveles, Bataan; Mindoro; and Batanes. The mineral is red. It has no economic value.

Ilmenite— $(Mg, Fe)TiO_3$ .

Ilmenite is found in black-sand concentrates in many streams throughout the Archipelago, usually in small crystals and more or less rounded grains. It is not utilized.

Iridium—Ir (metallic).

The occurrence of iridium is the same as osmium.

Jasper— $SiO_2$ .

Jasper occurs in fissile beds and in irregular masses. It contains remains of radiolarian tests. The color is brown to deep red.

**Kalinite (alum)**— $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$ .

Kalinite occurs in mealy crusts around solfataras at Taal Volcano and elsewhere; apparently in small quantities.

**Kaolinite**— $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .

Kaolinite occurs in the Philippines usually as a solfataric decomposition product of andesitic rocks; it is rarely pure. In the region around Laguna de Bay, Luzon, it is found in irregular "pockets." Kaolinite is used to a moderate extent in making pottery and for a local paint, so-called "yeso," which is the Spanish equivalent for gypsum.

**Labradorite**—(See Plagioclase).

**Leucite**— $\text{KAl}(\text{SiO}_3)_2$ .

Leucite occurs partially altered in certain very limited exposures of volcanic rock in the Aroroy district, Masbate. These rocks have from 8 to 10 per cent of potash, which might be made available for fertilizer.

**Lignite**—Various hydrocarbons.

Lignite is found in seams from 1 centimeter to 5 centimeters thick in many parts of the Archipelago. It usually crumbles into small cleavage cubes and air slacks. Its woody texture is seen best in weathered specimens. This mineral has been mined in the past, but there are no operations now.

**Limonite**.— $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ .

Limonite is associated with hematite and is found near the surface; it occurs also in small pisolitic granules. It is distributed in small amounts throughout the Archipelago. Sometimes limonite is used in small quantities for paint.

**Luzonite**— $\text{Cu}_3\text{AsS}_4$ .

Luzonite<sup>1</sup> is apparently a secondary ore of copper, and it is a special form of enargite. It forms in vugs and cracks in the vein. Luzonite is found in Mancayan, Mountain Province, and constitutes a large percentage of the enriched portion of the veins.

**Magnesite**— $\text{MgCO}_3$ .

Magnesite occurs associated with serpentine in Ilocos Norte as a white, earthy mineral, which is efflorescent. No use is made of it.

<sup>1</sup> Moses, *Am. Journ. Sci.* (1905), 277.



**Magnetite— $\text{Fe}_3\text{O}_4$ .**

Magnetite is widespread in small particles throughout the igneous rocks in the Philippines. It is also associated with the hematites of the Eastern Cordillera, Luzon. Fine octahedral crystals (No. 319) from San Miguel de Mayumo, Bulacan, Luzon, are in the collection of the Ateneo de Manila.

**Magnetized iron ore—Lode stone. Apparently iron oxides.**

This ore is found near Paracale, Camarines, and is also reported near Casiguran, Tayabas. No deposits are worked.

**Malachite— $(\text{Cu. OH})_2\text{CO}_3$ .**

No large crystalline samples of malachite are on record. This mineral is present in most of the copper deposits as a green coating.

**Manganite— $\text{MnO}(\text{OH})$ .**

Manganite occurs possibly with wad or pyrolusite in mineral veins, and often contains high values in gold. It is soft, and is derived from other manganese ores. It is found in several veins in Baguio and Suyoc, Mountain Province, and in Aroroy, Masbate. It has no economic value in the manner of its occurrence in the Philippines.

**Marcasite— $\text{FeS}_2$ .**

Marcasite is similar to pyrite, but is whiter. It is apparently infrequent. Marcasite has been reported from Mancayan, Luzon.

**Margarite— $\text{H}_2\text{CaAl}_4\text{Si}_2\text{O}_{12}$ .**

Margarite is a white mica occurring in certain schistose rocks of Ilocos Norte. No use is made of it, nor is there any production.

**Mercury— $\text{Hg}$  (metallic).**

Mercury is reported to occur in small crevices and pockets on Mount Isarog, Albay, Luzon. A small phial of it is in the museum of the Ateneo de Manila.

**Minium— $\text{PbO}$ .**

A large amorphous pink specimen of this mineral is in the museum of Santo Tomás University, marked "Filipinas;" no other data are given.

**Molybdenite— $\text{MoS}_2$ .**

Molybdenite is found in characteristic form in steel-blue flakes and leaves in quartz veins, Loboo Mountains, Batangas Province, Luzon. Only a small amount is found.

Muscovite— $K_2O \cdot 3Al_2O_3 \cdot 2H_2O$ .

Muscovite occurs rarely in igneous rocks. It occurs more commonly in schists, particularly in a quartz muscovite schist in Ambos Camarines. There are no economic deposits of this mineral in the Philippines.

Niter— $KNO_3$ .

Niter is said to be collected from certain caves on a small island near Surigao, Mindanao, and is used by natives for making gunpowder. This laboratory has no definite information regarding this substance in the Philippines, and its occurrence is to be doubted because of the heavy rainfall here.

Oligoclase—(See Plagioclase).

Olivine— $(Mg, Fe)_2SiO_4$ .

Olivine occurs in many rocks in the Islands, particularly in small greenish yellow grains in basalt and in so-called picrites of Panay. It is of no economic value.

Opal— $SiO_2 \cdot H_2O$ .

Opal is found in small fragments, and occasionally in large pieces of jasper. It occurs in Ilocos Norte and various other localities, but is not of any commercial value as found in the Philippines. One pretty specimen showing "fire" is in the museum of Santo Tomás University.

Orthoclase— $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ .

Orthoclase occurs sparingly in some igneous rocks. It is of no economic use.

Osmium—Os (metallic).

Osmium occurs with gold, iridium, and traces of platinum in thin metallic plates in decomposed rock. The locality where the mineral is found is said to be Luzon.

Petroleum—Complex series of hydrocarbons.

Petroleum occurs as a very light, paraffin-base oil in shales in various parts of the Islands, notably in Bondoc Peninsula, Tayabas, Luzon, and in Cebu. Two wells, one shallow and one deep, have yielded a small amount of oil.

Philippinite— $(K_2, Ca) Al_2Si_4O_{12} + 4\frac{1}{2}H_2O$ .

Philippinite occurs in characteristic white, radiating or tufted masses in Masbate. No economic use is made of it.

Pickeringite (magnesia alum)— $MgSO_4 \cdot Al_2(SO_4)_3 + 22H_2O$ .

Pickeringite is found in long fibrous masses as efflorescence

in the old Santa Barbara copper mine, Mancayan (Lepanto), Mountain Province, Luzon; it also occurs on Camaguin Island, north of Luzon.

**Plagioclase**—( $\text{NaAlSi}_3\text{O}_8$  to  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ).

This series of closely related minerals is one of the commonest of all the constituents of igneous rocks in the Philippines. It embraces the following species: Albite, anorthite, andesine, and labradorite. It has no known economic value as such.

**Platinum**—Pt (metallic).

Platinum is found in minute flattened grains in placer-test borings near Peñaranda in Nueva Ecija; on the Mariquina River in Rizal Province, Luzon; and in Agusan Valley, Mindanao. There is no production in the Philippines.

**Prochlorite**— $\text{H}_4(\text{Mg, Fe})_2\text{Al}_2\text{SiO}_9$ .

Prochlorite occurs in dirty green leaves which are flexible but not elastic. It is found in the metamorphic area of Ilocos Norte, Luzon. No use is made of it.

**Psilomelane**— $\text{H}_4\text{MnO}_5$ . The manganese is commonly replaced in part by barium or potassium.

Psilomelane occurs associated with pyrolusite. It is a very impure ore of manganese, often containing only 40 per cent of manganese (see Pyrolusite).

**Pyrite**— $\text{FeS}_2$ .

Pyrite occurs both massive and crystalline. The mineral appears as disseminated grains and as large crystals. Pyrite is often cupriferous. It is persistent in quartz veins and occasionally in calcite veins. Frequently it is one of the early minerals to crystallize. It is often associated with galena and zinc, but generally precedes them. Pyritization of vein walls occurs by reaction of the magnetite with  $\text{H}_2\text{S}$  gas from the fissure. Frequently this mineral is disseminated in volcanic rocks. Specimens of large secondary (?) crystals are in the Bureau of Science collection from Malaguit River, Camarines. Pyrite forms under conditions ranging from deep to surface. It is the most widely distributed metallic mineral. It is found in almost all rocks. This mineral is especially abundant in quartz veins, and is frequently associated with gold. There is no commercial use of pyrite in the Philippines.

**Pyrolusite**— $\text{MnO}_2$  with 2%  $\text{H}_2\text{O}$ .

Pyrolusite is the principal ore of manganese in the Philippines.

It occurs in botryoidal or massive shapes; also, reniform. It is found as veinlets in andesite and as nodules from erosion of veins and possibly in beds. It is found in Ilocos Norte, Pangasinan, Bulacan, Tarlac, and Masbate. It is not exploited.

**Pyroxene**— $\text{Ca (Mg, Fe) Si}_2\text{O}_6$ .

Pyroxene is a common constituent of pyroxene andesite, one of the chief rock types in the Islands. It occurs in small jet-black crystals. It has no economic value.

**Quartz**— $\text{SiO}_2$ .

Quartz is very persistent under conditions from deep seated to surface. It occurs in fine crystals in vugs under proper conditions; otherwise, it generally takes the form of jasper, chert, or siliceous sinter at the surface. It occurs in veins and as silicification of wall rocks. Two workable deposits only are known: (1) Siliceous spring deposits, Baguio, and (2) beach sand, Looc, Lubang Island. Quartz is used locally for road material and concrete in Baguio and at Looc.

**Realgar**— $\text{AsS}_2$ .

Realgar occurs as characteristic red crystals on a yellow coating of orpiment on pieces of slag (?) from the old Santa Barbara furnace at Mancayan, Luzon. As far as we know it does not occur in a natural state in the Philippines. Specimens, No. 59, of realgar are in the museum of the Ateneo de Manila.

**Rhodochrosite**— $\text{MnCO}_3$ .

Rhodochrosite occurs as a gangue mineral in auriferous calcite veins of Benguet. It is a primary mineral; it was probably leached from wall rocks by the ascending solutions and was later deposited with the calcite. Rhodochrosite is of no economic use.

**Rutile**— $\text{TiO}_2$ .

Microscopic crystals occur in some of the metamorphic rocks from Ilocos Norte associated with actinolite, muscovite, etc. Rutile has no economic value.

**Salt**— $\text{NaCl}$ .

Salt is deposited as incrustation from brackish carbonated springs in Mountain Province, Luzon, notably at Asin. It is used by the Igorots.

**Sanidine**— $(\text{K, Na}) \text{AlSi}_3\text{O}_8$ .

Sanidine occurs in small crystals and grains. This "glassy feldspar" is a dominant constituent of the andesites of many

peaks in Zambales Mountains and of Mount Apo, Mindanao. It is of no economic value.

**Sardonyx— $\text{SiO}_2$ .**

A specimen of this, No. 174, from Baganga, Mindanao, is in the collection of the Ateneo de Manila.

**Sericite— $3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .**

Sericite is one of the micas occurring in the schists of Ilocos Norte and Zamboanga Peninsula, Mindanao. It occurs in small gray-blue silky flakes. It is of no economic use.

**Serpentine— $\text{H}_2(\text{Mg, Fe})_3\text{Si}_2\text{O}_{10}$ .**

Serpentine, associated with pyroxenites and peridotites in more or less structureless masses, is found in Ilocos Norte and other localities. It is a greenish mineral. It occurs usually as asbestiform minerals. There is no production in the Philippines.

**Silvanite— $(\text{AuAg})\text{Te}_2$ .**

Silvanite occurs intimately mixed with the lead telluride altaite in quartz and calcite stringers in a contact between a slaty formation and a feldspar-porphyry dike.

**Silver—Ag (metallic).**

Silver occurs in the Philippines only in natural alloys with gold, and associated with the mineral galena. The gold from both placers and lodes in the Philippines carries silver varying in quantity up to 30 per cent. Silver-bearing galena is found at Panopoy, Cebu, and near Paracale, Camarines.

**Sphalerite— $\text{ZnS}$ .**

Sphalerite occurs massive or as small crystals, always associated with lead and pyrite. Like the other sulphides, it favors the quartz veins; it forms under conditions of moderate depth. It is found in practically all localities where galena is found (see Galena). Sphalerite is not found in economically valuable quantities in the Philippines, although widely found in many veins. It is not utilized.

**Stibnite— $\text{Sb}_2\text{S}_3$ .**

Stibnite occurs in characteristic fibrous masses. There is only one specimen in the Bureau of Science collection from Batangas Province, Luzon.

**Sulphur—S.**

Sulphur occurs more or less pure in characteristic yellow crystals around solfataras and also in a very impure state mixed with volcanic ash on Camiguin Island north of Luzon; on Taal Volcano and in Sorsogon, Luzon; on Mount Apo, Mindanao; and on Biliran Island. No sulphur is mined at present, but some mining was carried on formerly on Biliran.

**Talc— $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ .**

There are small amounts of talc associated with mica and actinolite in the metamorphic region of Ilocos Norte, Luzon. No local use is made of this mineral.

**Tetrahedrite— $4\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ .**

Tetrahedrite occurs as flint-gray to tin-black crystals. It is found at the old Santa Barbara mine, Mancayan, Lepanto, Luzon.

**Titanite— $\text{CaTiSiO}_5$  or  $\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$ .**

Titanite occurs as characteristic wedge-shaped crystals associated with the iron-ore deposits of Bulacan.

**Topaz— $(\text{AlF})_2\text{SiO}_4$  or  $(\text{Al}(\text{F}, \text{OH})_2)\text{SiO}_4$ .**

Topaz occurs in small (2-4 millimeters) pink, yellow, and colorless orthorhombic crystals. It is found in placers of Paracale River, Ambos Camarines.

**Tremolite— $\text{CaMg}_3(\text{SiO}_3)_4$ .**

Tremolite occurs in long white to greenish fibers associated with serpentine and asbestos in Ilocos Norte. It could be used commercially.

**Uralite—Composition same as pyroxene save for slight change in magnesium and calcium content.**

Uralite is a green alteration product of pyroxene, and is found in certain igneous rocks called metadiorites, which are altered gabbros.

**Vermiculite—Hydrated mica.**

Vermiculite is an earthy mica found in the metamorphic area of Ilocos Norte. It has no economic value.

**Wad—An earthy mixture of manganese oxides.**

Wad is found in association with psilomelane and pyrolusite. It is of no economic importance now.

**Wernerite**—Intermediate between  $\text{Ca}_4\text{Al}_6\text{Si}_6\text{O}_{25}$  and  $\text{Na}_4\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}$ .

Wernerite is a white fibrous silicate, and occurs in veinlets in greenstone in Aroroy district, Masbate. No economic use is made of it.

**Wolframite**— $(\text{FeMn})\text{WO}_4$ .

Wolframite is a heavy, black, crystalline mineral. Specimens are said to have been found in Antique Province, Panay. There is no economic development.

**Zeolite**—Composition is uncertain.  $\text{RAl}_2\text{Si}_{10}\text{O}_{24}$ .

Zeolite occurs as a fibrous secondary product in the decomposition of certain rock minerals, principally feldspars, and in amygdoloidal cavities throughout the Islands. This mineral has no known use.

## REVIEWS

A Laboratory Guide | to the Study of | Qualitative Analysis | based upon the | application of the theory of | electrolytic dissociation | and the law of mass action | by | E. H. S. Bailey, Ph.D. | professor of chemistry | and | Hamilton P. Cady, Ph.D. | associate professor of chemistry in the University of Kansas | seventh edition | Philadelphia | P. Blakiston's Son & Co. | 1012 Walnut Street | 1914 | Cloth, pp. i-x+1-280. Price, \$1.25 net.

The seventh edition of Professors Bailey and Cady's book is essentially the same as the sixth edition except that the alternative method for the treatment of the cations of groups III and IV which was an appendix in the sixth edition is in the present one incorporated in the body of the text.

The book contains a brief and accurate discussion of electrolytic dissociation and the mass law as applied to qualitative analysis; experiments and tables for the separation of cations and anions into groups and their identification; while such subjects as, hydrolysis, rules for oxidation and reduction, etc., are treated in their proper places in the book thereby making it easy for the student to comprehend their practical application. A table of solubilities closes the text. It is an excellent work for students of qualitative analysis in scientific schools of the Philippine Islands.

T. DAR JUAN.

The Source, Chemistry | and | Use of Food Products | by | E. H. S. Bailey, Ph.D. | professor of chemistry and director, Chemical Laboratories, | University of Kansas | author of "A system of quantitative analysis"; "Sanitary and | applied chemistry," etc. | with 75 illustrations | Philadelphia | P. Blakiston's Son & Co. | 1012 Walnut Street | No date, copyright, 1914. Price \$1.60 net.

The Source, Chemistry and Use of Food Products by E. H. S. Bailey of the University of Kansas is a book well adapted as a supplementary text in a high school or college course in agriculture or a course in dietetics.

It is a simple, readable, elementary text on the source and use of food products, containing numerous tables of the nutritive value of the foods described. It does not contain enough data on the chemistry of foods to be a complete text in this subject for college students; however, when supplemented by lectures it would be very valuable as reference reading.



The headings and subheadings are somewhat confusing because of their arrangement and frequency and we believe the appearance of the book would have been benefited by the adoption of a different system and by making fewer subheads. The data on any one particular food are also rather scattered and a closer correlation of this information would have resulted in an improved text. Many source references are given, which is a commendable feature, and while the references are limited in scope, they are the ones that are most apt to be available to the ordinary high school and college.

On the whole, the book is written in an interesting fashion, can be easily read by a person without a knowledge of chemistry, and, while it offers no new information on the subject of foods, is valuable because of its availability to the nontechnical person.

H. C. B.

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